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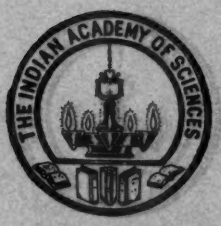


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# THE TETRAHEDRAL CARBON ATOM AND THE STRUCTURE OF DIAMOND*

By Sir C. V. Raman

(*Memoir No.* 104 *from the Raman Research Institute, Bangalore* 6)

## 1. Introduction

My address to the Academy this year concerns itself with the element carbon and its chemical behaviour. The importance of this subject hardly needs to be stressed. Indeed, the amazing power which the atoms of carbon display of combining with themselves and with other atoms to form an immense variety of distinct compounds is one of the marvels of nature. It is perhaps part of the secret of life itself.

The science of chemistry made a great step forwards when it was realised that the structure of a chemical molecule can only be properly described in terms of the configuration in three-dimensional space of the atoms of which it is composed. This approach to chemical problems made its debut in the year 1874 when Van'T Hoff put forward his famous hypothesis of the tetrahedral carbon atom. What that description of the carbon atom really signifies, the physical and chemical evidence on which our belief in its validity is based and the explanation of the chemical behaviour of carbon in terms of the ultimate structure of its atoms are the topics which we shall proceed to consider. The ideas which emerge from the discussion will then be applied to an elucidation of the crystal structure of diamond and the explanation of the properties of that remarkable substance.

## 2. The Four Valences of Carbon

The simplest molecules exhibiting the disposition in space of the valences of the carbon atom are those in which an atom of carbon combines with four similar atoms or similar groups of atoms. This situation exists, for example, in the cases of methane ($CH_4$), deuteromethane ($CD_4$), carbon tetrafluoride ($CF_4$), carbon tetrachloride ($CCl_4$), carbon tetrabromide ($CBr_4$), tetramethyl methane [$C(CH_3)_4$] and so forth. In all these cases, the atoms or atomic groups which combine with the carbon atom are found to be disposed in space with perfect tetrahedral symmetry round it. This is most convincingly shown by the study of the vibration spectra of these molecules.

* Presidential Address to the Indian Academy of Sciences at the Tirupati Meeting on the 28th December, 1957.

A molecule composed of five atoms would in general exhibit nine modes of free vibration. On the other hand, the five-atom groups listed above exhibit only four fundamental frequencies of vibration. Such a reduction would follow as a necessary consequence of the molecule possessing perfect tetrahedral symmetry. It is therefore to be regarded as demonstrating that the atoms in these molecules are located at the vertices of a regular tetrahedron with the carbon atom itself at its centre.

The vibration spectra of molecules in which an atom of carbon combines with three atoms of one kind and a fourth of a different kind show that in every such case, they have six fundamental vibration frequencies and no more. As examples of this behaviour may be listed the molecules of $DCH_3$, $HCD_3$, $HCF_3$, $FCH_3$, $HCCl_3$, $DCCl_3$, $FCCl_3$, $ClCH_3$, $ClCD_3$, $BrCH_3$, $BrCD_3$ and $ICH_3$. Dynamical theory shows that a five-atom group possessing a triad axis of symmetry would exhibit only six distinct frequencies instead of nine. The observed facts are thus a clear proof that the molecules listed do possess such a symmetry. On the other hand, molecules containing carbon combining with two atoms of one kind and two atoms of another kind should exhibit all the nine modes of vibration, and this is in agreement with experience.

The symmetry of form of the molecules in each of the cases referred to above can also be inferred from the numbers respectively of polarised and depolarised lines observed as frequency shifts in the spectra of light-scattering. Here again, the experimental facts confirm the tetrahedral character of the atomic grouping around the central carbon atom.

Studies on the vibration spectra of various molecules of the kind quoted above also furnish us with a convincing proof of the non-existence of the several isomers which may be expected to be forthcoming if the four valences of carbon were not equivalent. For, the vibration frequencies of the molecules would be influenced by the atomic configurations and each isomer would therefore have its own set of vibration frequencies. As the characteristic frequencies reveal themselves as well-defined lines in the spectrum, multiplication of the number of observed frequencies would follow as a consequence of the existence of more than one form of the molecule. As no such effect is observed in the numerous cases which have been studied, we are justified in inferring that such isomers do not exist.

A question of great importance which arises in regard to molecules in which an atom of carbon is joined to four others which are not all the same is whether their joins with it make equal angles with each other as is

to be expected if the valences were directed along the axes of a regular tetrahedron. This question can only be answered if methods for precise determination of the atomic configurations were available. Two such methods have been employed for the determination of the atomic configurations in molecules, namely, X-ray diffraction and electron diffraction. Both of these methods involve recondite theoretical considerations besides complicated calculations. The results derived from them must therefore be considered as subject to some measure of uncertainty and this has to be borne in mind in assessing the significance of the reported results. Pauling, in his book '*On the Nature of the Chemical Bond*' (Second Edition, 1940, Table 14-I) gives a list of sixteen carbon compounds of varying degrees of complexity whose molecular structure has been investigated by electron diffraction methods. The table of results gives the bond angle subtended at the carbon atom for eight different species of bonds, namely, C–C–C, C–C–Cl, C–C–Br, F–C–F, Cl–C–Cl, Br–C–Br, F–C–Cl and N–C–N. In five of these cases, namely, C–C–Br, C–C–Cl, F–C–F, F–C–Cl and N–C–N the angles are indistinguishable from the tetrahedral angle of 109° 28′, while in the three other cases, namely, Cl–C–Cl, C–C–C and Br–C–Br the reported bond angles exceed the tetrahedral angles by a degree or two; but this difference cannot be regarded as significant since the reported experimental uncertainties are of the same order of magnitude.

We may sum up the conclusions which may be legitimately drawn from the facts of experiment cited above as follows: *When an atom of carbon combines with four others, the four valences are directed along the four axes of a regular tetrahedron but are otherwise indistinguishable from each other.*

### 3. The Atomic Structure of Carbon

The interpretation which has to be placed on the results stated above becomes clear when we take note of the position of carbon in a list of the chemical elements arranged in the order of atomic numbers, that is to say, according to the magnitude of charge on the nucleus of the atom or the number of the electrons outside the nucleus. In such a list, the chemically inert gas helium occupies the second position, and the chemically inert neon occupies the tenth, while carbon with its six electrons occupies a position midway between them. Likewise, silicon which in several respects exhibits a chemical behaviour similar to carbon and has fourteen electrons stands midway between the inert gases neon and argon which have respectively ten and eighteen electrons outside their atomic nuclei. This is an example of the periodicity in chemical behaviour which makes itself evident when the elements are listed in the order of their atomic numbers. Such periodicity

finds its explanation in certain general features manifested in the building up of the atoms, *viz.*, the arrangement of the extra-nuclear electrons in a series of shells denoted respectively as K, L, M, etc. When the K shell is complete with its two electrons, we have the inert gas helium; when the L shell is also complete with its eight additional electrons, we have the inert gas neon; when a further eight electrons have been put into the M shell, we have the inert gas argon. Thus it is clear that the quadrivalence of carbon arises from the fact that it has four electrons in the L shell, just half the full quota of eight electrons needed to complete that shell. Further, since the valences are directed along the four axes of a regular tetrahedron, we are evidently concerned here with a state of the atom in which the four electrons in the L shell by reason of their interactions with each other and with the force field of the charged core of the atom constitute a system which is electrically neutral but exhibits perfect tetrahedral symmetry. This system may therefore be rightly designated as the tetrahedral carbon atom. It can combine with four other atoms or groups of atoms to form molecules, but does not depart sensibly from its tetrahedral symmetry of structure as the result of such combination.

We have now to ask ourselves what precisely are the circumstances which favour the formation of the tetrahedral quartet of electrons referred to above. It is well known that helium, neon and argon besides being chemically inert are also diamagnetic in their behaviour. The explanation given for the latter circumstance is that in the building up of the electronic clouds, the magnetic moments arising from the inherent spins of the electrons as well as those, if any, arising from their orbital movements around the nucleus mutually cancel each other out. The same circumstance is also responsible for the chemical inertness of these gases. For this to happen in the L shell of an atom we require eight electrons, but since there are only four present in the L shell of carbon, the same situation cannot arise in its case. But the question does arise as to how the angular momenta associated with the orbital motion and the inherent spins of the four electrons are disposed. If the configuration resulting from the mutual interactions of the four electrons is to possess full tetrahedral symmetry, it is clearly necessary that the resultant angular momenta associated with each of the four electrons considered individually should be equal and that further, these momenta should set themselves respectively along the four axes of a regular tetrahedron. The total angular momentum of the quartet and hence also its magnetic moment would vanish in these circumstances, and hence *the quartet of electrons must be considered as diamagnetic. But it would not*

*be chemically inert since the cancellation is a result of the tetrahedral setting of the individual angular momenta and not of their internal pairing off.*

An interesting consequence of the foregoing ideas should be here referred to. The angular momentum of an electron and hence also the magnetic moment associated with it is a vector and hence must be regarded as having both a direction and a sign. As already remarked, the directions in the present case are along the four axes of a regular tetrahedron, and if the quartet is to possess tetrahedral symmetry, all the four vectors concerned should have the same sense. Hence, they should all be directed either outwards or inwards from the core of the atom. Thus we have two distinct possible states of the tetrahedral carbon atom which we might designate as the $\alpha$ and the $\beta$ states respectively. These do not differ from each other except in the sense of the angular momenta of the individual electrons, these being directed respectively outwards or inwards from the charged core of the atom in the two cases.

## 4. The Crystal Structure of Diamond

Diamond furnishes a perfect illustration of Van'T Hoff's hypothesis of the tetrahedral carbon atom. For, X-ray analysis discloses its structure to consist of two sets of carbon atoms, each carbon atom in one set being chemically linked with perfect tetrahedral symmetry to four carbon atoms belonging to the other set and *vice versa*. The joins of the carbon atom in each set with the four others in the second set are all parallel to each other and to the four body-diagonals of a cube. Hence diamond exhibits the symmetry belonging to a crystal of the cubic class. Considering this situation in the light of the remarks made in the preceding section, it follows that diamond is a crystal whose properties would not be uniquely decided by the crystal structure alone as determined by the methods of X-ray analysis. Diamond consists of two interpenetrating lattices of carbon atoms. In an ideal crystal all the atoms belonging to one lattice should be the same, but as there are two possible types of tetrahedral carbon atom, it follows that an ideal diamond may belong to any one of four types, namely, $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$. There is no reason to expect that these four types of diamond would exhibit any significant differences in such properties as lattice spacings, or the energy of formation, or the atomic vibration frequencies and so forth. But we should expect observable differences of a less obvious kind arising from the fact that the $\alpha\alpha$ and $\beta\beta$ types of diamond would possess a perfect octahedral symmetry in their crystal structure, whereas the two other types $\alpha\beta$ and $\beta\alpha$ would exhibit only the lower or tetrahedral symmetry.

Thus our present approach to the basic problems of organic chemistry leads to a natural and intelligible explanation of the fact that some diamonds exhibit infra-red absorption in the region of wave-lengths about 8 $\mu$ including the characteristic lattice frequencies of vibration, while other diamonds do not exhibit this absorption. The diamonds which exhibit such absorption are those whose structure is of the $\alpha\beta$ or $\beta\alpha$ type, while those that do not are those whose structure is of the $\alpha\alpha$ or $\beta\beta$ type. Considerations of the same nature would also account for the differences exhibited by diamond in respect of other properties including expecially the presence or absence of absorption of light in the near ultra-violet, which as is well known accompany the presence or absence of infra-red absorption in the 8 $\mu$ region. We shall not enter into these questions here in detail but shall content ourselves with making two further remarks. The difference between the diamonds exhibiting octahedral and tetrahedral symmetry respectively cannot be expected to manifest itself in any difference in piezo-electric behaviour. The other remark is to recall the fact long known to mineralogists that the external forms of the diamond crystals found in nature more often than not indicate the lower or tetrahedral symmetry instead of the higher or octahedral one. This fact ceases to be surprising in the light of the considerations set forth above.

## 5. THE THEORY OF HYBRID BOND ORBITALS

We cannot avoid making some reference here to the attempts that have been made to explain the directed valences of the carbon atom in terms of ideas based on the Schrodinger solution of the wave-equation for the hydrogen atom. The theory of hybrid bond orbitals, as it is called, can be summarised as follows: The solution of the hydrogen problem by the Schrodinger method yields a series of solutions (*s*, *p*, *d*, etc.) which indicate the possible distributions of electron density around the nucleus. The wave-function *s* indicates a distribution of electron density spherically symmetrical round the nucleus, where there are three wave-functions denoted by $p_x$, $p_y$ and $p_z$ respectively which represent density distributions whose maximum extensions are respectively along the *x*, *y* and *z* axes in both directions. All these wave-functions represent the same energy and hence it is possible to construct linear combinations of them so as to produce new wave-functions which are orthogonal to each other. By giving equal weights to the wave-functions $p_x$, $p_y$ and $p_z$ but different signs in different cases and adding the *s* wave-function, it is possible to obtain four wave-functions which are tetrahedrally symmetric with respect to the nucleus,

The four orbitals thus derived are put forward as a representation of the directed valences of a carbon atom.

Several criticisms of a fundamental nature regarding the theory thus briefly summarised may be put forward. The first objection is that we are not concerned here with a hydrogen atom having a single electron but with a carbon atom having two inner and four outer electrons; the interactions of these with each other and with the atomic nucleus are of the very essence of the problem but they are left out of consideration in the theory. A second objection is that the theory does not explicitly consider the spin of the electrons, though they play a fundamental role in the theory of atomic structure. Apart from these difficulties, one is also confronted with the fact that we have an infinite number of possible $sp^3$ hybrids and the question may well be asked why the particular set which gives four orbitals indicative of a tetrahedral orientation of the valences should be chosen out of them all. The fundamental feature of the quadrivalence of carbon is that the tetrahedral disposition of the valences is maintained even when the four atoms with which the combination occurs differ from each other enormously, as for example, hydrogen, carbon, nitrogen, fluorine, bromine, chlorine and iodine—to mention no others. *It is this circumstance which indicates that the determining factor which gives rise to the tetrahedral configuration of the valences is not the energy of formation of the bond or bonds, but is an inherent property of the carbon atom itself.* In other words, it is to be found in the mutual interactions between the quartet of electrons which compel them to set themselves in a uniquely determined tetrahedral configuration.

## 6. Summary

The experimental evidence derived from the study of the vibration spectra of molecules and of their electron diffraction patterns shows unequivocally that the four valences directed outwards from a carbon atom are parallel to the four axes of a regular tetrahedron. That this disposition is maintained even when the four atoms combining with the carbon atom differ enormously from each other indicates that we are concerned here with an intrinsic property of the carbon atom, namely, that the quartet of electrons in the L shell as a result of their mutual interactions can set themselves so as to constitute a structure possessing perfect tetrahedral symmetry. Such a structure would be diamagnetic but not chemically inert, since the individual angular momenta cancel out as a result of the tetrahedral setting and not as a consequence of the internal pairing off as in the inert gas molecules.

It follows from these considerations that there are two possible states of the carbon atom and hence also four possible forms of diamond, which may be designated as $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$ and $\beta\beta$ respectively. The first and the last would have true octahedral symmetry, while the second and the third would have the lower or tetrahedral symmetry. The differences in physical behaviour exhibited by even ideal diamonds in various respects, including especially their infra-red absorption spectra, thus receive a natural and intelligible explanation.

# TEMPERATURE DEPENDENCE OF PHOTO-ELASTIC CONSTANTS IN ALKALI HALIDES

By S. Bhagavantam, F.A.Sc. and Y. Krishna Murty

Received November 14, 1957

## 1. Introduction

In an earlier paper (1956) published in these *Proceedings*, we reported the influence of temperature on the photo-elastic behaviour of some plastics. It seemed worthwhile to extend such studies to cubic crystals also as there has so far been very little work done along these lines. The present paper is concerned with alkali halides.

## 2. Experimental

All the crystal prisms used in this investigation have been specially cut and polished. None of the prisms showed double refraction in the unstrained state. A full description of the prisms is given in Table I. The alkali halides studied belong to the $O_h$ class of the cubic system and in all the cases, the value of $(q_{11} - q_{12})$ was obtained from prism I when stress was applied along [001] and observation made along [010]; and $q_{44}$ was obtained from prism II when stress was applied along [110] and observation made along [001].

Table I

*Description of the prisms employed*

| | No. of prism | Length | | Breadth | | Thickness | |
|---|---|---|---|---|---|---|---|
| | | Cm. | Parallel to | Cm. | Parallel to | Cm. | Parallel to |
| NaCl .. | I | 1·550 | [001] | 0·762 | [010] | 0·673 | [100] |
| | II | 1·129 | [110] | 0·598 | [$\bar{1}$10] | 0·471 | [001] |
| KCl .. | I | 0·838 | [001] | 0·512 | [010] | 0·412 | [100] |
| | II | 1·110 | [110] | 0·731 | [$\bar{1}$10] | 0·617 | [001] |
| KBr .. | I | 1·556 | [001] | 0·635 | [010] | 0·564 | [100] |
| | II | 1·162 | [110] | 0·549 | [001] | 0·523 | [$\bar{1}$10] |

The stress-optical coefficients of rock salt are small when compared with those of potassium chloride and potassium bromide. Further, it is known that plastic deformation takes place in rock salt when the load exceeds about 20·0 kg./cm.$^2$ Due to the above limitations, the Babinet compensator does not give an appreciable shift and a Rayleigh compensator was employed to determine the photo-elastic coefficients of NaCl at different temperatures. The experimental set-up and method of observation are essentially the same as those employed by Narasimhamurty (1954). The Rayleigh compensator is very sensitive and may be made to measure a birefringence of the order of 1/500 λ. The crystal prism must be well polished so that the dark band may be seen clearly. For each temperature, the prism of rock salt crystal was loaded after the temperature remained fairly constant.

The comparatively higher values of potassium halides have enabled the Babinet compensator being used in determining their photo-elastic coefficients at various temperatures. The Babinet-fringes were obtained by the usual method using a sodium vapour lamp as the source. Compression was produced by a lever arrangement described in an earlier paper (1947). Stresses of the order of 35·0 kg./cm.$^2$ were applied in the case of KCl and KBr. Final measurements were taken only when it was ascertained that load was uniformly distributed. The mean shift of the Babinet-fringe in each case was obtained by taking the average of several readings. The path retardation read in terms of the head-scale divisions of the Babinet compensator is a measure of the birefringence produced in the crystal prisms.

In order to study the variation of the induced birefringence with temperature a robust electrical heater was built, the crystal prism being centrally situated within the enclosure. By means of a variac, the voltage could be varied slowly and steadily till the requisite temperature was attained. The temperature was maintained at the higher level for about four hours and then brought back to room temperature over a period of about another four to five hours. In this way, development of permanent strains in the crystals was avoided. Measurements of fringe shifts in both the cases were made at intervals of 50° C., temperatures being read by a suitable thermometer.

In evaluating the photo-elastic coefficients at different temperatures, the refractive index as well as the thickness perpendicular to the direction of observation were to be determined for each temperature. The values of the coefficients of thermal expansion for NaCl, KCl and KBr were deduced utilising the formulæ given by Walther and others (1937), Durand (1936) and Srinivasan (1956) respectively. The refractive indices at higher temperatures for NaCl and KCl were evaluated from the values of $dn/dt$ given by

Ramachandran (1947). Data are, however, not available in literature regarding the thermo-optic behaviour of KBr. Hence a plane parallel plate of KBr of thickness 0·2 cm. had been prepared and the refractive indices at higher temperatures obtained by the usual interference method. The values of refractive indices at various temperatures for the three alkali halides used in the present work are shown in Table II.

TABLE II

*Values of* $n_D$ *at different temperatures*

| Temp. °C. | NaCl | KCl | KBr |
|---|---|---|---|
| 30 | 1·5440 | 1·4903 | 1·55983 |
| 100 | 1·5414 | 1·4880 | 1·55557 |
| 150 | 1·5395 | 1·4860 | 1·55280 |
| 200 | 1·5377 | 1·4840 | 1·55004 |
| 250 | 1·5358 | 1·4820 | 1·54728 |
| 300 | 1·5339 | 1·4800 | 1·54451 |
| 350 | 1·5320 | .. | .. |

## 3. Results and Discussion

*Sodium Chloride*

The results are given in detail in Tables III A and III B.

TABLE III A

*Measurements with Rayleigh compensator for NaCl prism No.* I

| Temp. °C. | Mean shift in Rayleigh | Retardation in Å. | $(q_{11}-q_{12})$ $\times 10^{13}$ | $(c_{11}-c_{12})$ $\times 10^{-11}$ | $(p_{11}-p_{12})$ $\times 10^{2}$ |
|---|---|---|---|---|---|
| 30 | 14·0 | 305·6 | 1·13 | 3·663 | 4·13 |
| 100 | 13·0 | 283·8 | 1·06 | 3·353 | 3·54 |
| 175 | 12·0 | 262·0 | 0·99 | 3·068 | 3·02 |
| 250 | 11·2 | 245·0 | 0·93 | 2·802 | 2·61 |
| 350 | 10·3 | 224·8 | 0·86 | 2·475 | 2·13 |

TABLE III B

*Measurements with Rayleigh compensator for NaCl prism No. II*

| Temp. °C. | Mean Shift in Rayleigh | Retardation in Å. | $(q_{44})$ $\times 10^{13}$ | $(c_{44})$ $\times 10^{-11}$ | $(p_{44})$ $\times 10^{2}$ |
|---|---|---|---|---|---|
| 30 | 7·0 | 152·8 | 0·84 | 1·281 | 1·07 |
| 125 | 6·4 | 139·7 | 0·77 | 1·250 | 0·97 |
| 250 | 5·3 | 115·7 | 0·65 | 1·205 | 0·78 |
| 350 | 4·6 | 100·4 | 0·57 | 1·170 | 0·67 |

The values of stress-optical coefficients $(q_{11} - q_{12})$ and $q_{44}$ are both negative in sign for NaCl and the magnitudes are found to decrease linearly with temperature. This is in accordance with the decrease in its elastic constants. The strain-optical coefficients are calculated from the standard equation connecting the $p$'s, $q$'s and the elastic constants. The data on elastic constants for NaCl are available from Hunter and Siegal (1942).

*Potassium Chloride and Potassium Bromide*:

The results obtained are given in Tables IV and V. The fringe width of the Babinet compensator is 470·5 divisions of the head-scale, which corresponds to a path retardation of one wavelength of sodium light.

TABLE IV A

*Measurements with Babinet-compensator for KCl prism No. I*

| Temp. °C. | Mean shift in divisions of head-scale | $(q_{11}-q_{12})$ $\times 10^{13}$ | $(c_{11}-c_{12})$ $\times 10^{-11}$ | $(p_{11}-p_{12})$ $\times 10^{2}$ |
|---|---|---|---|---|
| 30 | 41·6 | 1·66 | 3·41 | 5·65 |
| 100 | 43·9 | 1·76 | 3·22 | 5·67 |
| 150 | 45·7 | 1·85 | 3·07 | 5·67 |
| 200 | 48·7 | 1·98 | 2·94 | 5·83 |
| 250 | 52·3 | 2·14 | 2·82 | 6·03 |
| 300 | 55·7 | 2·30 | 2·70 | 6·20 |

TABLE IV B

*Measurements with Babinet-compensator for KCl prism No. II*

| Temp. °C. | Mean shift in divisions of head-scale | $q_{44}$ $\times 10^{13}$ | $c_{44}$ $\times 10^{-11}$ | $p_{44}$ $\times 10^{2}$ |
|---|---|---|---|---|
| 30 | 124·7 | 4·42 | 0·630 | 2·78 |
| 100 | 129·4 | 4·61 | 0·620 | 2·86 |
| 150 | 131·3 | 4·71 | 0·612 | 2·88 |
| 200 | 133·4 | 4·80 | 0·603 | 2·90 |
| 250 | 136·1 | 4·94 | 0·594 | 2·94 |
| 320 | 141·1 | 5·17 | 0·580 | 3·00 |

TABLE V A

*Measurements with Babinet compensator for KBr prism No.* I

| Temp. ° C. | Mean shift in divisions of head-scale | $(q_{11}-q_{12})$ $\times 10^{13}$ | $(c_{11}-c_{12})$ $\times 10^{-11}$ | $(p_{11}-p_{12})$ $\times 10^{2}$ |
|---|---|---|---|---|
| 30 | 58·9 | 1·73 | 2·86 | 4·94 |
| 100 | 62·8 | 1·86 | 2·67 | 4·98 |
| 150 | 66·0 | 1·97 | 2·47 | 4·87 |
| 200 | 69·7 | 2·10 | 2·36 | 4·95 |
| 250 | 73·7 | 2·24 | 2·24 | 5·01 |
| 300 | 78·4 | 2·40 | 2·13 | 5·12 |

From the mean shift of the Babinet-fringe, the path difference corresponding to unit stress (1 dyne cm.$^{-2}$) and unit length (1 cm.) of light beam

TABLE V B

*Measurements with Babinet compensator for KBr prism No.* 1

| Temp. °C. | Mean shift in divisions of head-scale | $(q_{44})$ $\times 10^{12}$ | $(c_{44})$ $\times 10^{-11}$ | $(p_{44})$ $\times 10^{2}$ |
|---|---|---|---|---|
| 30 | 133·5 | 4·72 | 0·504 | 2·38 |
| 100 | 137·2 | 4·91 | 0·498 | 2·45 |
| 150 | 140·4 | 5·06 | 0·494 | 2·50 |
| 200 | 142·8 | 5·18 | 0·488 | 2·53 |
| 250 | 145·4 | 5·32 | 0·482 | 2·57 |

in the stressed crystal was calculated. The stress-optical coefficient in the corresponding direction of observation is $2\delta/n^3$. The sign of $(q_{11} - q_{12})$ is positive and that of $q_{44}$ is negative in the case of KCl and KBr. In both these substances, the stress-optical coefficients are found to increase with temperature, the variation being nearly linear in the case of $(q_{11} - q_{12})$ and linear for $q_{44}$. Also the variation is much greater in $(q_{11} - q_{12})$ than in $q_{44}$. The values of the strain-optical coefficients are calculated in the same manner as for NaCl. The data on elastic constants of KCl and KBr at different temperatures have been obtained by Subrahmanyam (1954).

## 4. SUMMARY

The paper furnishes measurements on the birefringence produced at different temperatures in crystals of NaCl, KCl and KBr when subjected to stress. The results show that the stress-optical coefficients $(q_{11} - q_{12})$ and $q_{44}$ decrease in the case of NaCl almost linearly with temperature while in KCl and KBr they increase with the same. The variation for rock salt is of the order of about 30% over an interval of 300° C. In both KCl and KBr, the variation in $(q_{11} - q_{12})$ which is about 40% over the same interval of temperature is much greater than in $q_{44}$ which is of the order of about 15%. The corresponding strain-optical coefficients are also evaluated and given at each temperature.

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# STUDIES IN THE ISOQUINOLINE SERIES

## Part III. Synthesis of Some 5 : 6—and 5 : 8—Dimethoxyisoquinolines

By T. R. Govindachari, F.A.Sc. and Miss M. V. Lakshmikantham

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Although papaverine is a valuable antispasmodic drug used in current clinical practice, the search for a better spasmolytic drug has never abated. Eupapaverine[1] and Neupaverine[2] are products of this effort. Several 1-dialkoxyphenyl and 1-dialkoxyphenethyl isoquinolines have been shown to have considerable spasmolytic activity.[3] It has been claimed that 3-methylisoquinolines have lowered toxicity than the 3-unsubstituted analogues. The work reported in this paper forms part of a programme of work on spasmolytic drugs in progress in this laboratory.[4]

β-(2 : 5-Dimethoxyphenyl) ethyl amine[5] was prepared by the lithium aluminium hydride reduction of 2 : 5-dimethoxy-ω-nitrostyrene. Its formyl, acetyl, benzoyl and phenylacetyl derivatives were smoothly cyclised by phosphorus oxychloride to 3 : 4-dihydro-5 : 8-dimethoxy-, 3 : 4-dihydro-5 : 8-dimethoxy-1-methyl-, 3 : 4-dihydro-5 : 8-dimethoxy-1-phenyl-, and 3 : 4-dihydro-5 : 8-dimethoxy-1-benzylisoquinolines respectively.

Similarly, from β-(2 : 5-dimethoxyphenyl) isopropyl amine,[6] prepared by the lithium aluminium hydride reduction of 2 : 5-dimethoxy-β-methyl-ω-nitrostyrene, the corresponding 3 : 4-dihydro-3-methylisoquinolines were prepared.

β-(2 : 3-Dimethoxyphenyl) ethyl amine[7] was prepared by the reduction of 2 : 3-dimethoxy-ω-nitrostyrene. β-2 : 3-dimethoxyphenylisopropyl amine was prepared by the Hofmann degradation of β-2 : 3-dimethoxyphenyl-α-methyl-propionamide. The formyl, acetyl, benzoyl and phenylacetyl derivatives of these amines were cyclised to the corresponding 3 : 4-dihydro- and 3 : 4-dihydro-3-methylisoquinolines.

Reduction of 2 : 4-dimethoxy-ω-nitrostyrene and of 2 : 4-dimethoxy-β-methyl-ω-nitrostyrene with lithium aluminium hydride led to 2 : 4-dimethoxyphenylethyl amine and 2 : 4-dimethoxyphenylisopropyl amine respectively. The amides derived from either of these amines could not be made to yield the corresponding 3 : 4-dihydro-5 : 7-dimethoxyisoquinolines under any condition. The cumulative inductive deactivation of the position of cyclisation by both the methoxyl groups which are meta to this position should be res-

ponsible for this failure. A single methoxyl group meta to the point of cyclisation has been shown to inhibit ring closure.[8]

All the 3-methyl-3:4-dihydroisoquinolines underwent dehydrogenation with remarkable facility by heating in decalin solution with palladised charcoal (5% Pd). Dehydrogenation of 3:4-dihydroisoquinolines with a substituent at the 1-position, but not having a substituent at the 3-position, was more difficult, requiring a higher temperature and longer duration. Dehydrogenation of 3:4-dihydroisoquinolines without a substituent either at the 3- or 1-positions could not be effected using palladised charcoal, but was achieved only with palladium black as catalyst.

## Experimental Procedure

*ω-Nitrostyrenes.*—These were prepared by the following procedure which is illustrated in the case of 2:5-dimethoxy-β-methyl nitrostyrene.

A mixture of 2:5-dimethoxybenzaldehyde (10 g.), nitroethane (10 ml.), glacial acetic acid (50 ml.) and ammonium acetate (4 g.) was refluxed for 3 hr. The solution was cooled and poured into ice-water. The precipitate was collected, washed and dried to yield the nitrostyrene (12 g.) which crystallised from dilute acetic acid in yellow needles, m.p. 78–79° (Found: C, 59·0; H, 6·1; N, 6·6. $C_{11}H_{13}O_4N$ requires C, 59·2; H, 5·8; N, 6·3%).

2:4-Dimethoxybenzaldehyde (15 g.) was treated similarly with nitroethane (15 ml.), ammonium acetate (6 g.) and acetic acid (60 ml.) to yield 2:4-dimethoxy-β-methylnitrostyrene (18 g.), light yellow crystals from dilute acetic acid, m.p. 83° (Found: C, 59·2; H, 5·8; N, 6·3%).

By a similar procedure was obtained 2:5-dimethoxynitrostyrene, m.p. 120°, 2:3-dimethoxynitrostyrene, m.p. 88° and 2:4-dimethoxynitrostyrene, m.p. 108°. The melting points were in agreement with those reported in literature.

*β-Phenylethylamines.*—The following procedure illustrated in the case of β-(2:4-dimethoxyphenyl) isopropyl amine was adopted for all the amines, except β-(2:3-dimethoxyphenyl) isopropyl amine:

A solution of 2:4-dimethoxy-β-methylnitrostyrene (9 g.) in ether (150 ml.) was dropped into a suspension of lithium aluminum hydride (4 g.) in ether (150 ml.) during 2 hr. After stirring for 1 more hr., water was added to decompose the reaction mixture and the ether decanted off and extracted with hydrochloric acid (3 × 50 ml.; 2 N). The combined acid extracts were made basic with aqueous sodium hydroxide and extracted with ether. The ether extract was dried over potassium hydroxide and evaporated. The residue was distilled *in vacuo* to yield β-(2:4-dimethoxyphenyl) isopropyl amine

(4·5 g.), b.p. 147°/4 mm., $n^{30°}$ 1·512, yielding a hydrochloride, colourless needles from alcohol-ether, m.p. 147°.

β-(2: 5-Dimethoxyphenyl) ethyl amine, b.p. 160°/10 mm., $n^{30°}$ 1·524, β-(2: 5-dimethoxyphenyl) isopropyl amine, b.p. 148°/3 mm., β-(2: 3-dimethoxyphenyl) ethyl amine, b.p. 136–138°/5 mm., and β-(2:4-dimethoxyphenyl) ethyl amine, b.p. 143°/3 mm., $n^{30°}$ 1·344 were thus obtained from the corresponding nitrostyrenes.

The following procedure was adopted for β-(2: 3-dimethoxyphenyl)-isopropyl amine:

2: 3-*Dimethoxy-α-methylcinnamic acid.*—A mixture of 2: 3-dimethoxybenzaldehyde (40 g.), propionic anhydride (32 ml.) and fused sodium propionate (24 g.) was heated at 145° for 48 hr. The mixture was treated with a slight excess of 4 N sodium hydroxide, boiled and filtered. The cooled filtrate was shaken with benzene (3 × 60 ml.) and then acidified with concentrated hydrochloric acid. Crystallisation of the precipitate (41 g.) from alcohol gave 2: 3-dimethoxy-α-methylcinnamic acid, m.p. 113° (Found: C, 64·6; H, 6·4. $C_{12}H_{14}O_4$ requires C, 64·9; H, 6·3%).

β-(2: 3-*Dimethoxyphenyl*)-α-*methylpropionic acid.*—The above cinnamic acid (30 g.) was dissolved in the calculated quantity of N sodium hydroxide and reduced with sodium amalgam (5%; 500 g.) added in portions, with occasional additions of hydrochloric acid to keep the medium neutral. The aqueous layer was separated and acidified. The precipitated oil gradually solidified to give the propionic acid (28 g.), which crystallised from petroleum ether, melted at 57° (Found: C, 64·4; H, 7·1. $C_{12}H_{16}O_4$ requires C, 64·3,H, 7·1%).

β-(2: 3-*Dimethoxyphenyl*)-α-*methylpropionamide.*—A solution of the above acid (44 g.) in dry benzene (150 ml.) was left aside with thionyl chloride (32 ml.) for 24 hr., and poured into liquor ammonia (700 ml.) containing sodium hydroxide (10 g.) with stirring at 0°. Stirring was continued for 1hr., after the addition was over. The solid (34g.) that separated was filtered, washed and dried. On recrystallising from hot water, the amide melted at 85° (Found: C, 64·6; H, 7·0, N, 6·3. $C_{12}H_{17}O_3N$ requires C, 64·6; H, 7·6; N, 6·3%).

β-(2: 3-*Dimethoxyphenyl*) *isopropyl amine.*—The above amide (7·5 g.) in dioxane (30 ml.) was added at 0° to sodium hypochlorite solution (prepared by passing chlorine from 3 g. potassium permanganate into 12 g. sodium hydroxide dissolved in 100 g. ice and 20 g. water) and stirred at 0° for 1 hr. The solution was warmed to 50°, treated with solid potassium hydroxide (25 g.) and maintained at 70° for 1 hr. It was then cooled and

extracted with benzene. The benzene layer was shaken with hydrochloric acid (250 ml.; 1 N). The acid layer was separated, cooled, basified and extracted with ether. The ether layer was dried, and evaporated and the residue distilled *in vacuo* to give the isopropyl amine (1·5 g.), b.p. 125°/1 mm., yielding a hydrochloride, which on crystallisation from alcohol-ether, melted at 154°.

*β-Phenylethylamides.*—Formyl derivatives were made by heating the amine with 95% formic acid for 3 hr., at 180°, and isolating the neutral product. Acetyl derivatives were obtained by refluxing the amine for ½–1 hr., with acetic anhydride and dilution with ice-water. Benzoyl and phenylacetyl derivatives were obtained by the Schotton-Baumen procedure, using the appropriate acid chloride.

The formyl and acetyl derivatives of β-(2: 3-dimethoxyphenyl)-ethyl and isopropylamines were obtained as oils and were used as such for cyclisation. The other amides are listed in Table I.

3: 4-*Dihydroisoquinolines.*—The procedure adopted for cyclisation of the amides is illustrated in the case of N-acetyl-β-(2: 5-dimethoxyphenyl)-ethyl amine.

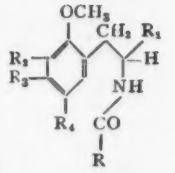
A solution of the acetamide (0·95 g.) in dry toluene (9 ml.) and phosphorus oxychloride (4 ml.) was refluxed for 2 hr., and poured into crushed ice. After some time, the aqueous layer was separated, and the toluene extracted with hydrochloric acid (10 ml.; 4 N). The combined acid extracts were shaken once with ether, cooled, basified and extracted with ether. The ether extract was dried over anhydrous potassium carbonate and evaporated to yield the dihydroisoquinoline (0·76 g.) as a yellow oil which solidified on standing.

The dihydroisoquinolines were characterised mainly as the picrates; some of them were obtained as solids by crystallisation or vacuum sublimation. Table II records relevant data.

None of the derivatives of β-(2: 4-dimethoxyphenyl) ethyl- and isopropyl amines could be cyclised.

*Isoquinolines.*—The procedure used for dehydrogenating the dihydroisoquinolines is illustrated in the case of 3: 4-dihydro-5: 8-dimethoxy-3-methylisoquinoline.

The dihydroisoquinoline (0·3 g.) was dissolved in decalin (50 ml.) and heated with palladised charcoal (5%, 0·1 g.) at 180–90° for 7 hr., in an atmosphere of carbon dioxide till no more hydrogen was evolved. The



I

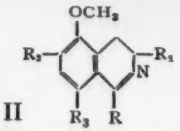
TABLE I

*β-Phenylethylamides*

| R | $R_1$ | $R_2$ | $R_3$ | $R_4$ | Molecular formula | M.P. ° C. | Found % | | | Required % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | C | H | N | C | H | N |
| H | H | H | H | OMe | $C_{11}H_{15}O_3N$ | 70 | 62·7 | 7·0 | 6·8 | 63·1 | 7·2 | 6·7 |
| Me | H | H | H | OMe | $C_{12}H_{17}O_3N$ | 99–100[9] | .. | .. | .. | .. | .. | .. |
| Ph | H | H | H | OMe | $C_{17}H_{19}O_3N$ | 86 | 71·4 | 6·4 | 5·0 | 71·6 | 6·7 | 4·9 |
| $PhCH_2$ | H | H | H | OMe | $C_{12}H_{21}O_3N$ | 105 | 72·4 | 7·2 | 4·9 | 72·2 | 7·0 | 4·7 |
| H | Me | H | H | OMe | $C_{19}H_{17}O_3N$ | 78 | 64·4 | 7·5 | 6·3 | 64·6 | 7·6 | 6·3 |
| Me | Me | H | H | OMe | $C_{13}H_{19}O_3N$ | 111–112[10] | .. | .. | 6·2 | .. | .. | 6·2 |
| Ph | Me | H | H | OMe | $C_{18}H_{21}O_3N$ | 155–156 | 72·3 | 7·2 | 4·5 | 72·2 | 7·0 | 4·9 |
| $PhCH_2$ | Me | H | H | OMe | $C_{19}H_{23}O_3N$ | 137 | 73·2 | 6·9 | 4·5 | 72·9 | 7·3 | 4·5 |
| Ph | H | OMe | H | H | $C_{17}H_{19}O_3N$ | 86 | 71·3 | 6·7 | 4·8 | 71·6 | 6·7 | 4·9 |
| $PhCH_2$ | H | OMe | H | H | $C_{18}H_{21}O_3N$ | 112 | 72·4 | 7·2 | 4·5 | 72·2 | 7·0 | 4·7 |
| Ph | Me | OMe | H | H | $C_{18}H_{21}O_3N$ | 70 | 72·6 | 6·8 | 4·9 | 72·2 | 7·0 | 4·7 |
| $PhCH_2$ | Me | OMe | H | H | $C_{19}H_{23}O_3N$ | 81 | 72·5 | 7·5 | 4·5 | 72·9 | 7·3 | 4·6 |
| Ph | H | H | OMe | H | $C_{17}H_{19}O_3N$ | 115 | .. | .. | 5·0 | .. | .. | 4·9 |
| $PhCH_2$ | H | H | OMe | H | $C_{18}H_{21}O_3N$ | 134 | .. | .. | 4·7 | .. | .. | 4·7 |
| Me | Me | H | OMe | H | $C_{13}H_{19}O_3N$ | 96 | 65·7 | 7·7 | 6·0 | 65·8 | 8·0 | 5·9 |
| Ph | Me | H | OMe | H | $C_{18}H_{21}O_3N$ | 132 | 72·1 | 6·9 | 4·7 | 72·2 | 7·0 | 4·7 |
| $PhCH_2$ | Me | H | OMe | H | $C_{19}H_{23}O_3N$ | 120 | 72·3 | 7·2 | 4·6 | 72·9 | 7·3 | 4·5 |

TABLE II

*Picrates of* 3 : 4-*Dihydroisoquinolines*




II

| R | $R_1$ | $R_2$ | $R_3$ | Molecular formula | M.P. °C. | Found % | | | Required % | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C | H | N | C | H | N |
| H | H | H | OMe | $C_{17}H_{16}O_9N_4$ | 160 | 48·8 | 3·7 | 13·5 | 48·6 | 3·8 | 13·3 |
| Me | H | H | OMe | $C_{18}H_{18}O_9N_4$[a] | 189 | 49·3 | 4·5 | 13·1 | 49·7 | 4·1 | 12·9 |
| Ph | H | H | OMe | $C_{23}H_{20}O_9N_4$[b] | 195 | 55·8 | 3·8 | 11·5 | 55·6 | 4·0 | 11·3 |
| $PhCH_2$ | H | H | OMe | $C_{24}H_{22}O_9N_4$ | 165 | 56·5 | 4·3 | 11·1 | 56·5 | 4·3 | 11·0 |
| H | Me | H | OMe | $C_{15}H_{18}O_9N_4$ | 203 | 49·4 | 3·7 | 13·2 | 49·8 | 4·1 | 12·9 |
| Me | Me | H | OMe | $C_{23}H_{25}O_7N_5$[c] | 186 | .. | .. | 14·8 | .. | .. | 14·5 |
| Ph | Me | H | OMe | $C_{24}H_{22}O_9N_4$[d] | 181 | 56·9 | 4.2 | 11·1 | 56·5 | 4·3 | 11·0 |
| $PhCH_2$ | Me | H | OMe | $C_{25}H_{24}O_9N_4$ | 152 | 56·9 | 4·4 | 10·7 | 57·3 | 4·6 | 10·7 |
| H | H | OMe | H | $C_{17}H_{16}O_9N_4$ | 185 | 48·8 | 3·6 | 13·3 | 48.6 | 3·8 | 13·3 |
| Me | H | OMe | H | $C_{22}H_{23}O_7N_5$[e] | 234 | 56·5 | 5·3 | 14·8 | 56·3 | 4·9 | 14·9 |
| Ph | H | OMe | H | $C_{23}H_{20}O_9N_4$[f] | 162 | 55·8 | 3·7 | 11·5 | 55·6 | 4·0 | 11·3 |
| $PhCH_2$ | H | OMe | H | $C_{24}H_{22}O_9N_4$ | 172 | 56·1 | 4.4 | 10·8 | 56·5 | 4·3 | 11·0 |
| H | Me | OMe | H | $C_{18}H_{18}O_9N_4$ | 182 | 50·0 | 4·1 | 12·8 | 49·8 | 4·1 | 12·9 |
| Me | Me | OMe | H | $C_{19}H_{20}O_9N_4$ | 146 | 51·1 | 4·8 | 12·7 | 50·9 | 4·5 | 12·5 |
| Ph | Me | OMe | H | $C_{24}H_{22}O_9N_4$ | 149 | 56·1 | 4·2 | 11·1 | 56·5 | 4·3 | 11·0 |
| $PhCH_2$ | Me | OMe | H | $C_{25}H_{24}O_9N_4$ | 149 | 57·2 | 4·4 | 10·7 | 57·3 | 4·6 | 10·7 |

[a] Free base, m.p. 68° (*cf.* Sugasawa and Shigehara[9]).
[b] Free base, m.p. 99° (Found: C, 76·7; H, 6·4; N, 5·4. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%).
[c] Picrolonate; hydrochloride, m.p. 177° (*cf.* Govindachari and Pai[4]).
[d] Base, m.p. 129° (Found: C, 77·1; H, 6·9; N, 4·9. $C_{18}H_{19}O_2N$ requires C, 76·9; H, 6·8; N, 4·9%); hydrochloride, m.p. 2 05°. (decomp.) (Found: C, 67·9; H, 6·4; N, 4·4. $C_{18}H_{20}O_2NCl$ requires C, 68·0; H, 6·3; N, 4·4%).
[e] Picrolonate; picrate, m.p. 215° (decomp.) (*cf.* Rajagopalan[10]).
[f] Base, m.p. 105° (Found: C, 75·9; H, 6·4; N, 5·5. $C_{17}H_{17}O_2N$ requires C, 76·4; H, 6·4; N, 5·2%).

TABLE

*Iso*

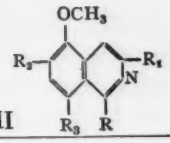
| R | $R_1$ | $R_2$ | $R_3$ | BASE | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Molecular Formula | M.P. °C. | Found % | | | Required % | | |
| | | | | | | C | H | N | C | H | N |
| H .. | H | H | OMe | $C_{11}H_{11}O_2N$ | 58 | 69·5 | 5·9 | .. | 69·8 | 5·8 | .. |
| Me .. | H | H | OMe | $C_{12}H_{13}O_2N$ | 54 | 70·9 | 6·2 | .. | 70·9 | 6·4 | .. |
| Ph .. | H | H | OMe | $C_{17}H_{15}O_2N$ | 124 | 76·7 | 5·7 | 5·4 | 77·0 | 5·7 | 5·3 |
| $PhCH_2$ | H | H | OMe | $C_{18}H_{17}O_2N$ | 89 | 77·9 | 6·2 | 5·1 | 77·4 | 6·1 | 5·0 |
| H .. | Me | H | OMe | $C_{12}H_{13}O_2N$ | 77 | 71·1 | 6·2 | .. | 70·9 | 6·4 | .. |
| Me .. | Me | H | OMe | $C_{13}H_{15}O_2N \cdot H_2O$ | 70 | 66·0 | 7·2 | 6·0 | 66·4 | 7·2 | 6·0 |
| Ph .. | Me | | OMe | $C_{18}H_{17}O_2N$ | 118 | 77·0 | 6·0 | 5·2 | 77·4 | 6·1 | 5·0 |
| $PhCH_2$ | Me | H | OMe | $C_{19}H_{19}O_2N$ | 114 | 78·2 | 6·8 | 4·8 | 77·8 | 6·5 | 4·8 |
| H .. | H | OMe | H | $C_{11}H_{11}O_2N$ | 40 | .. | .. | .. | .. | .. | .. |
| Me .. | H | OMe | H | $C_{12}H_{13}O_2N$ | 93 | 70·4 | 6·1 | 7·2 | 70·9 | 6·4 | 6·9 |
| Ph .. | H | OMe | H | $C_{17}H_{15}O_2N$ | 112 | 77·2 | 5·6 | 5·3 | 77·0 | 5·7 | 5·3 |
| $PhCH_2$ | H | OMe | H | .. | .. | .. | .. | .. | .. | .. | .. |
| H .. | Me | OMe | H | $C_{12}H_{13}O_2N$ | 85 | 70·5 | 6·6 | 7·1 | 70·9 | 6·4 | 6·9 |
| Me .. | Me | OMe | H | .. | .. | .. | .. | .. | .. | .. | .. |
| Ph .. | Me | OMe | H | $C_{18}H_{17}O_2N$ | 85 | 77·1 | 6·2 | .. | 77·4 | 6·0 | .. |
| $PhCH_2$ | Me | OMe | H | $C_{19}H_{19}O_2N$ | 134 | 77·5 | 6·8 | 4·9 | 77·8 | 6·5 | 4·8 |

[a] Picrolonate; Base hydrochloride, m.p. 234° (Found: C, 57·4; H, 6·9; N, 5·5.
[b] Base hydrochloride, m.p. 166° (Found: C, 67·8; H, 5·7; $C_{18}H_{18}O_2NCl$ requires C, 68·3;
[c] Base hydrochloride, m.p. 209° (decomp.) (Found: C, 68·6; H, 6·3; N, 3·9. $C_{19}H_{20}O_2NCl$
[d] Picrolonate.

decalin solution was filtered and the catalyst washed with benzene (10 ml). The combined filtrates were repeatedly extracted with hydrochloric acid (3×25 ml.; 4 N). The acid extracts were cooled, basified and extracted with ether. The ether extract was dried and evaporated to leave the isoquinoline (0·2 g.).

III

*quinolines*




III

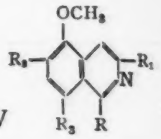
PICRATE

| Mol. Formula | M.P. °C. | Found % | | | Required % | | |
|---|---|---|---|---|---|---|---|
| | | C | H | N | C | H | N |
| $C_{17}H_{44}O_9N_4$ | 210 (decomp.) | .. | .. | 13·3 | .. | .. | 13·4 |
| $C_{18}H_{16}O_9N_4$ | 237 (decomp.) | 50·4 | 3·4 | 12·7 | 50·0 | 3·7 | 12·9 |
| $C_{23}H_{18}O_9N_4$ | 202 | 56·2 | 3·6 | 11·3 | 55·9 | 3·6 | 11·3 |
| $C_{24}H_{20}O_9N_4$ | 215 | 56·3 | 4·1 | 11·1 | 56·7 | 3·9 | 11·0 |
| $C_{18}H_{16}O_9N_4$ | 243 (decomp.) | 49·7 | 3·9 | 12·9 | 50·0 | 3·7 | 12·9 |
| $C_{23}H_{23}O_7N_5 \cdot H_2O$[a] | 230 | .. | .. | 13·8 | .. | .. | 14·0 |
| $C_{24}H_{20}O_9N_4$[b] | 178 | 57·2 | 4·0 | .. | 56·7 | 3·9 | .. |
| $C_{25}H_{22}O_9N_4$[c] | 176 | 56·9 | 3·9 | 10·4 | 57·5 | 4·2 | 10·7 |
| $C_{17}H_{14}O_9N_4$ | 211 | 48·5 | 3·2 | 13·0 | 48·8 | 3·3 | 13·4 |
| $C_{22}H_{21}O_7N_5$[d] | 245 | 56·9 | 5·0 | 15·0 | 56·5 | 4·5 | 15·0 |
| $C_{23}H_{18}O_9N_4$ | 168 | 55·5 | 3·8 | 11·2 | 55·9 | 3·6 | 11·3 |
| $C_{24}H_{20}O_9N_4$ | 208 | 56·4 | 3·7 | 11·0 | 56·7 | 3·9 | 11·0 |
| $C_{18}H_{16}O_9N_4$ | 241 | 50·1 | 3·5 | 13·3 | 50·0 | 3·7 | 13·0 |
| $C_{19}H_{18}O_9N_4$[e] | 184 | 50·8 | 3·8 | 12·5 | 51·1 | 4·0 | 12·6 |
| $C_{24}H_{20}O_9N_4$ | 180 | 56·6 | 4·2 | 10·7 | 56·7 | 3·9 | 11·0 |
| $C_{25}H_{22}O_9N_4$ | 162 | 57·8 | 4·0 | .. | 57·5 | 4·2 | .. |

$C_{13}H_{16}O_2NCl \cdot H_2O$ requires C, 57·5; H, 6·6; N, 5·2%); (*cf.* Govindachari and Pai[4]).
H, 5·7%).
requires C, 68·7; H, 6·0; N, 4·2%).
[e] *cf.* Govindachari and Pai[4].

Palladised charcoal in decalin at 210–40° was used for dehydrogenating dihydroisoquinolines with a substituent at 1-position and none at 3. For 1:3-unsubstituted dihydroisoquinolines, palladium black in decalin at 200° was required. The isoquinolines were purified by crystallisation or sublimation or regeneration from pure derivatives. In this manner all the

isoquinolines except 5:6-dimethoxy-, 5:6-dimethoxy-3-methyl-, and 5:6-dimethoxy-1:3-dimethylisoquinolines were obtained as crystalline solids. The appropriate data are summarised in Table III. The u.v. absorption data are recorded in Table IV.




IV

TABLE IV

| R | $R_1$ | $R_2$ | $R_3$ | $\lambda_{max}$ in mμ | log $\epsilon_{max}$ |
|---|---|---|---|---|---|
| H | H | H | OMe | 220, 240, 245, 250, *276–277*, 283, 320, 330, 350 | 4·3, 4·22, 4·26, 4·17, 3·88, 3·81, 3·99, 3·86, 3·88 |
| Me | H | H | OMe | 245, 335 | 4·07, 3·83 |
| Ph | H | H | OMe | 214·5, 322, 325 | 4·4, 3·79, 3·82 |
| $PhCH_2$ | H | H | OMe | *248–249*, 335 | 4·21, 3·84 |
| H | Me | H | OMe | 225, 249–250, 325, *346–348*, 350 | 4·27, 4·24, 3·62, 3·71, 3·71 |
| Me | Me | H | OMe | 225, 250, 315, 345 | 4·12, 4·04, 3·77, 3·81 |
| Ph | Me | H | OMe | 253, 320, *322–325*, *352–354* | 4·14, 3·85, 3·85, 3·85 |
| $PhCH_2$ | Me | H | OMe | 254, *319–322*, 350 | 4·16, 3·78, 3·79 |
| H | H | OMe | H | *237–238*, 255, 300, 310, 365 | 4·72, 3·73, 3·68, 3·67, 2·55 |
| Me | H | OMe | H | 240, 305 | 4·64, 3·70 |
| Ph | H | OMe | H | 230, 234, 236, *310–315* | 4·50, 4·55, 4·65, 3·82 |
| $PhCH_2$ | H | OMe | H | 236, 238, 241, 244, 305 | 4·67, 4·68, 4·66, 4·68, 3·79 |
| H | Me | OMe | H | 236, 238, *240–241*, 305 | 4·71, 4·73, 4·71, 3·65 |
| Me | Me | OMe | H | 241, 243, 304 | 4·64, 4·64, 3·63 |
| Ph | Me | OMe | H | 231, 235, 311, *316–318*, 330 | 4·56, 4·65, 3·86, 3·84, 3·84 |
| $PhCH_2$ | Me | OMe | H | 242, 246, *310–315* | 4·69, 4·69, 3·67 |

## Summary

A series of 3:4-dihydro-5:6-dimethoxy and 3:4-dihydro-5:8-dimethoxyisoquinolines are reported. These have been dehydrogenated to the corresponding isoquinoline derivatives.



## Acknowledgement

We are thankful to the Government of Madras for a scholarship to one of us (M.V.L.).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# EMISSION SPECTRUM OF BROMINE EXCITED IN THE PRESENCE OF ARGON

## Part II. The Band System in the Region 3150–2970 Å

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ABSTRACT

The wavelengths and wavenumbers of the band heads of the system 3150–2970 Å as obtained from the plates taken on the first order 21′ grating spectrograph are given along with the vibrational analysis. This system is shown to be due to a transition from an upper electronic state at $T_e = 48516$ cm.$^{-1}$ with $\omega'_e = 162{\cdot}0$ cm.$^{-1}$ and $\omega'_e\chi'_e = 0{\cdot}29$ cm.$^{-1}$ to the well-known $^3\Pi_u$ ($O_u^+$) state at $T_e = 15918$ cm.$^{-1}$ This lower state is common with that of the system 2950–2670 Å.

### INTRODUCTION

BROMINE when excited in the presence of argon was reported in an earlier paper[1] by the present authors to give: (1) a short discrete band system in the region 3150–2970 Å, (2) an extensive discrete band system in the region 2950–2670 Å, (3) a short and weak discrete band system in the region 2660–2590 Å and (4) a set of diffuse bands in the region 3340–3190 Å. The band system in the region 2950–2670 Å was analysed and discussed in that paper. The present paper deals with the analysis and discussion of the band system 3150–2970 Å.

### EXPERIMENTAL RESULTS

Using the same experimental set-up and conditions as described in the earlier paper, the band system 3150–2970 Å was photographed with a 21′ grating spectrograph in the first order and also with a Hilger $E_1$ Littrow quartz spectrograph. This system is weaker than the 2950–2670 Å system discussed in the earlier paper and a part of it is usually overlapped by the traces of OH lines in the region 3064–3150 Å. It was, however, possible to get one plate without any trace of OH lines, but this plate showed only the intense part of the system.

The wavelengths and wavenumbers of the bands as measured from the plates taken on the 21′ grating spectrograph are given in Table I along with

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their visually estimated relative intensities. The degradation of the bands in the system is not as clear as that in the 2950–2670 Å system. This may be because the vibrational frequencies of the upper and lower states for this system are much nearer to one another than those for the 2950–2670 Å. system. Some of the bands appear to be degraded to long wavelength side and some towards short wavelength side while most of the bands do not appear to show any degradation. The error involved in the measurements of the band heads may be $\pm 4$ or $\pm 5$ cm.$^{-1}$

TABLE I

*Wavelengths, wavenumbers and relative intensities of the bands in the system* λ 3150–2970 *Å*

| I | $\lambda_{air}$ | $\nu_{vac.}$ | I | $\lambda_{air}$ | $\nu_{vac.}$ |
|---|---|---|---|---|---|
| 4 | 3140·4 | 31834 | 4 | 3087·4 | 32380 |
| 4 | 3138·5 | 31853 | 4 | 3083·5 | 32421 |
| 1 | 3136·3 | 31875 | 4 | 3082·7 | 32430 |
| 4 | 3134·1 | 31898 | 1 | 3076·2 | 32498 |
| 5 | 3132·5 | 31914 | 1 | 3069·5 | 32569 |
| 5 | 3131·1 | 31928 | 1 | 3067·1 | 32595 |
| 6 | 3126·7 | 31973 | 2 | 3060·1 | 32669 |
| 6 | 3125·1 | 31990 | 1 | 3058·8 | 32683 |
| 8 | 3122·5 | 32016 | 4 | 3057·7 | 32695 |
| 4 | 3121·8 | 32024 | 4 | 3057·2 | 32700 |
| 4 | 3120·4 | 32038 | 4 | 3056·6 | 32706 |
| 8 | 3119·9 | 32052 | 4 | 3054·3 | 32731 |
| 8 | 3118·4 | 32058 | 2 | 3053·9 | 32736 |
| 1 | 3117·2 | 32071 | 4 | 3052·4 | 32752 |
| 5 | 3113·8 | 32106 | 4 | 3052·1 | 32755 |
| 6 | 3112·1 | 32123 | 4 | 3050·7 | 32768 |
| 10 | 3110·7 | 32138 | 4 | 3050·3 | 32775 |
| 4 | 3109·1 | 32154 | 0 | 3049·2 | 32786 |
| 8 | 3106·9 | 32177 | 0 | 3048·1 | 32798 |
| 8 | 3105·1 | 32196 | 4 | 3047·0 | 32810 |
| 6 | 3101·2 | 32237 | 4 | 3046·3 | 32817 |
| 6 | 3099·3 | 32256 | 5 | 3045·0 | 32831 |
| 6 | 3098·6 | 32263 | 5 | 3044·4 | 32837 |
| 6 | 3097·5 | 32275 | 0 | 3043·0 | 32853 |
| 6 | 3096·8 | 32282 | 0 | 3041·4 | 32870 |
| 4 | 3095·9 | 32291 | 3 | 3039·8 | 32887 |
| 5 | 3095·2 | 32299 | 3 | 3037·8 | 32909 |
| 6 | 3093·4 | 32318 | 3 | 3037·0 | 32918 |
| 7 | 3091·5 | 32337 | 1 | 3036·4 | 32924 |
| 4 | 3090·2 | 32351 | | | |

TABLE I (*Contd.*)

| I | $\lambda_{air}$ | $\nu_{vac.}$ | I | $\lambda_{air}$ | $\nu_{vac.}$ |
|---|---|---|---|---|---|
| 1 | 3035·7 | 32932 | 0 | 3009·4 | 33220 |
| 1 | 3034·3 | 32947 | 2 | 3008·1 | 33234 |
| 1 | 3033·7 | 32953 | 1 | 3006·5 | 33252 |
| 0 | 3031·8 | 32974 | 1 | 3005·0 | 33268 |
| 2 | 3030·3 | 32990 | 1 | 3002·4 | 33297 |
| 2 | 3029·8 | 32996 | 1 | 3000·7 | 33316 |
| 1 | 3025·8 | 33040 | 2 | 2998·2 | 33344 |
| 1 | 3023·1 | 33069 | 2 | 2995·5 | 33374 |
| ? | 3021·9 | 33082 | 2 | 2994·8 | 33382 |
| 1 | 3021·0 | 33092 | 2 | 2994·2 | 33388 |
| 2 | 3018·7 | 33117 | 1 | 2986·9 | 33470 |
| 1 | 3016·6 | 33140 | 2 | 2981·4 | 33532 |
| 2 | 3014·4 | 33164 | 1 | 2976·0 | 33592 |
| 2 | 3012·8 | 33182 | 0 | 2967·1 | 33693 |
| 1 | 3009·9 | 33214 | | | |

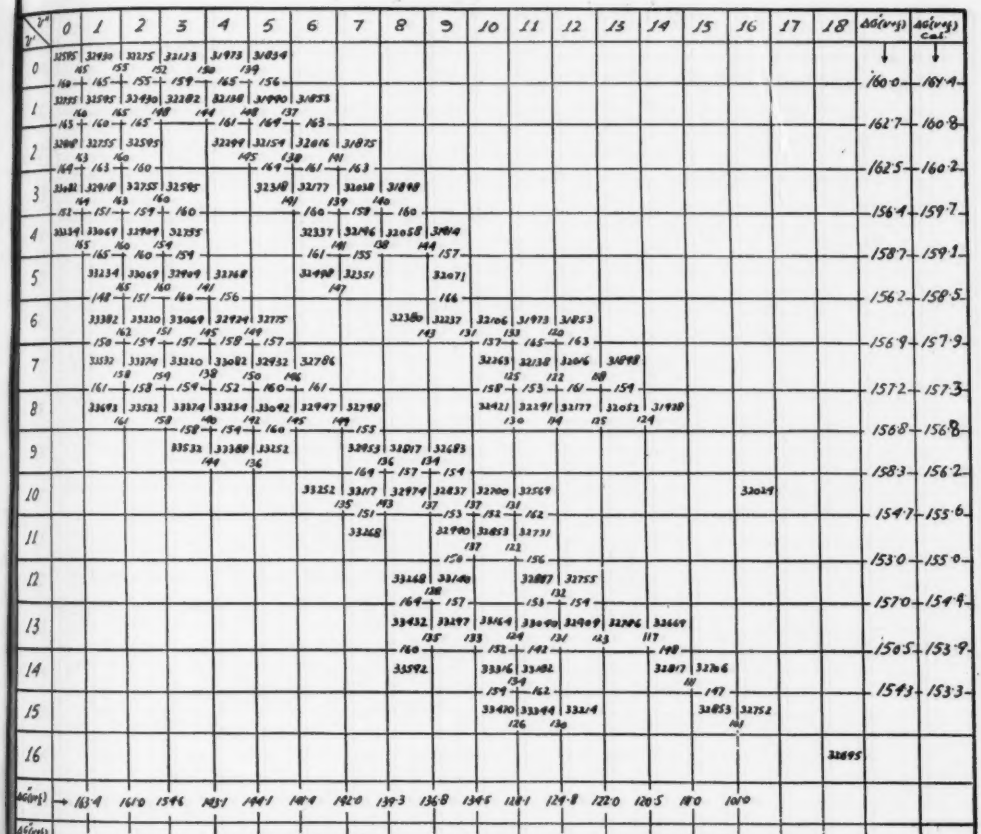
## THE VIBRATIONAL ANALYSIS

The vibrational analysis of the system is shown in Table II and the Frank-Condon parabola representing the intensity distribution in Table III. The analysis shows that all the bands in the system could be well represented as involving a transition from an upper initial state at $T_e = 48516$ cm.$^{-1}$ to the lower state at $T_e = 15918$ cm.$^{-1}$ with the same $\triangle G''(v + \frac{1}{2})$ as given by Darbyshire[2] and Brown.[3] This state at 15918 cm.$^{-1}$ is the well-known $^3\Pi_u$ ($O_u^+$) state which forms the upper state of the visible absorption band system[2] in the region 8672–5110 Å and is also the lower state of the band system 2950–2670 Å discussed in the earlier paper.

The $\triangle G''(v + \frac{1}{2})$ and $\triangle G'(v + \frac{1}{2})$ values as obtained from the analysis are shown in Table II. The $\triangle G(v + \frac{1}{2})$ values for the $^3\Pi_u$ ($O_u^+$) level as obtained by Darbyshire and Brown from the visible absorption band system and those as obtained by the present authors from the analysis of the 2950–2670 Å system are included in Table II for comparison. The existence of perturbation of $v = 3$ and $v = 4$ for the vibrational levels of the $^3\Pi_u$ ($O_u^+$) state was indicated by Darbyshire[2] from the analysis of the visible absorption band system and is confirmed by the analysis of the present system as well as by that of the 2950–2670 Å system. Because of this perturbation it will not be possible to find a single formula of the usual type representing accurately all the band heads in the system. However the vibrational constants of the two electronic states involved in the transition could be obtained fairly well

TABLE II

*The vibrational scheme for the band system λ 3150–2970 Å*



from the observed $\triangle G(v + \frac{1}{2})$ values following the usual procedure. The vibrational constants $\omega_0'' = 166 \cdot 1$ cm.$^{-1}$ and $\omega_0'' x_0'' = 1 \cdot 84$ cm.$^{-1}$ obtained by Darbyshire from the analysis of the visible absorption band system are found to represent well the observed $\triangle G''(v + \frac{1}{2})$ values of the present system as in the case of the 2950–2670 Å system. The observed $\triangle G'(v + \frac{1}{2})$ values could be represented fairly well by the vibrational constants $\omega_0' = 161 \cdot 7$ cm.$^{-1}$

TABLE III

*The intensity distribution and Frank-Condon parabola of the bands in the system* λ 3150–2970 Å

| v′ \ v″ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 1 | 4 | 6 | 6 | 6 | 4 | | | | | | | | | | | | | |
| 1 | 4 | 1 | 4 | 6 | 10 | 6 | 4 | | | | | | | | | | | | |
| 2 | 3 | 4 | 1 | | 5 | 4 | 8 | 1 | | | | | | | | | | | |
| 3 | ? | 3 | 4 | 1 | | 6 | 8 | 4 | 4 | | | | | | | | | | |
| 4 | 2 | 1 | 3 | 4 | | | 7 | 8 | 8 | 5 | | | | | | | | | |
| 5 | | 2 | 1 | 3 | 4 | | 1 | 4 | | 1 | | | | | | | | | |
| 6 | | 2 | 0 | 1 | 1 | 4 | | | 4 | 6 | 5 | 6 | 4 | | | | | | |
| 7 | | 2 | 2 | 0 | ? | 1 | 0 | | | | 6 | 10 | 8 | 4 | | | | | |
| 8 | | 0 | 2 | 2 | 2 | 1 | 1 | 0 | | | 4 | 4 | 8 | 8 | 5 | | | | |
| 9 | | | | 2 | 2 | 1 | | 1 | 4 | 1 | | | | | | | | | |
| 10 | | | | | | | 1 | 2 | 0 | 5 | 4 | 1 | | | | | 4 | | |
| 11 | | | | | | | | 1 | | 2 | 0 | 4 | | | | | | | |
| 12 | | | | | | | | | 1 | 1 | | 3 | 4 | | | | | | |
| 13 | | | | | | | | | ? | 1 | 2 | 1 | 3 | 0 | 2 | | | | |
| 14 | | | | | | | | | 1 | | 1 | 2 | | | 5 | 4 | | | |
| 15 | | | | | | | | | | | 1 | 2 | 1 | | | 0 | 4 | | |
| 16 | | | | | | | | | | | | | | | | | | | 4 |

and $\omega_0'x_0' = 0{\cdot}29$ cm.$^{-1}$ The calculated $\triangle G'\ (v + \frac{1}{2})$ values are included in Table II for comparison.

## ISOTOPIC SHIFTS

As the vibrational frequencies for the upper and the lower states are not much different from one another, the isotopic shifts calculated for most of the bands observed do not come out to be more than 2 or 3 cm.$^{-1}$ which is within the experimental error of the measurements. This may be the main reason why no isotopic shifts could not be detected, though one expects two

weak isotopic components for each main band. Another probable reason why the isotopic shifts were not observable is that the band system is weak and a part of the system is overlapped by the OH lines.

## Electronic Transition Involved

The lower state of this 3150–2970 Å system like that of the 2950–2670 Å system described in the earlier paper is $\sigma_g{}^2\pi_u{}^4\pi_g{}^3\sigma_u\,{}^3\pi_u\,(O_u{}^+)$.

It is difficult to say definitely which electronic state is involved for the upper state unless the rotational structure of the bands of the system is studied, but the spectrum obtained in the present experiments does not show any rotational structure. However, as pointed out in the earlier paper with the help of the term scheme developed by Mulliken[4] for the iodine molecule and later on extended by Asundi and Venkateswarlu[5] for bromine molecule, the only configuration which is expected to give *gerade* states at about 50,000 cm.$^{-1}$ is $\sigma_g{}^2\pi_u{}^2\pi_g{}^4\sigma_u{}^2$. This configuration gives the states $^1\Sigma_g{}^+\,(O_g{}^+)$ $^3\Sigma_g{}^-\,(O_g{}^+,\,1_g)$ and $^1\triangle_{2g}$ of which the last one cannot combine with the $^3\Pi_u\,(O_u{}^+)$ state as the coupling is expected to be near that of Hund's case (*c*). $^1\Sigma_g{}^+\,(O_g{}^+)$ is expected to lie higher than $^3\Sigma_g{}^-\,(O_g{}^+,\,1_g)$ and it had been tentatively attributed to the state at $T_e = 51802$ cm.$^{-1}$ which forms the upper level of the band system 2950–2670 Å. $^3\Sigma_g{}^-\,(O_g{}^+$ or $1_g)$ may be tentatively assigned to the state at $T_e = 48516$ cm.$^{-1}$ which forms the upper state of the present system 3150–2970 Å. This state may also be expected to be ionic like the $^1\Sigma_g{}^+\,(O_g{}^+)$ state at 51802 cm.$^{-1}$

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# VERTICAL IONOSPHERIC SOUNDINGS AT AHMEDABAD DURING TOTAL SOLAR ECLIPSE ON 30th JUNE 1954

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(Communicated by Dr. Vikram A. Sarabhai, F.A.SC.)

On June 30, 1954, there occurred a solar eclipse at Ahmedabad (23° 02′ N., 72° 38′ E.). Ahmedabad lay to the south of the shadow track. As the eclipse occurred late in the evening it was considered that the characteristics of the eclipse would not be the same at different levels above the ground. The times and phases of the eclipse at heights of 0, 100, 200 and 300 km. above Ahmedabad were therefore calculated. The results are given in Table I.

Table I

*Characteristics of the eclipse of* 30 *June* 1954 *at Ahmedabad*

| Height above the ground | 0 km. | 100 km. | 200 km. | 300 km. |
|---|---|---|---|---|
| Time of the beginning of the eclipse | 1807·4 | 1808·4 | 1809·5 | 1810·7 |
| Time of maximum phase of the eclipse | 1859·3 | 1858·3 | 1857·2 | 1856·2 |
| Magnitude of the eclipse | 93% | 94% | 97% | 99·8% |
| Time of Sunset | 1859 | 1944 | 2004 | 2021 |

The times are given as 75° E.M.T.

It is seen that though there was not much difference in the times of the various phases of the eclipse at different heights, the eclipse at 300 km. was almost total whereas at ground level it was only 93%. The times of sunset at different heights were, of course, different. At ground level the sun had set at the time of maximum obscuration, but at greater heights, the sun had begun to be uncovered before it went below the horizon.

The British N.P.L. type automatic ionospheric height recorder installed in the laboratory was used for all the measurements. On the control days, P′-*f* records were taken every fifteen minutes from 16 hr. to 21 hr.

75° E.M.T. On the eclipse day, once every fifteen minutes observations were started at 1030 hr.; the recordings were more frequent afterwards and during the eclipse, records were taken once every five minutes.

*The lower layers.*—As during the eclipse the solar altitude was very low, the ionisation of the lower layers was decreasing rapidly with decreasing cos $\chi$ of the sun. The eclipse therefore could not be of much use to study the lower layers of the ionosphere. The critical frequencies of E, $E_2$ and $F_1$ layers, and the minimum virtual heights of the $F_1$ layer on the eclipse day and on the control days are shown in Fig. 1. The E layer reflection traces on the eclipse day were often merged with those of Es and so $h'$E is not shown on the diagram. As expected, the critical frequencies of E and $F_1$ decreased at a faster rate after the start of the eclipse. The $E_2$ layer showed changes similar to $F_1$, but the effect of the eclipse is not very clear.

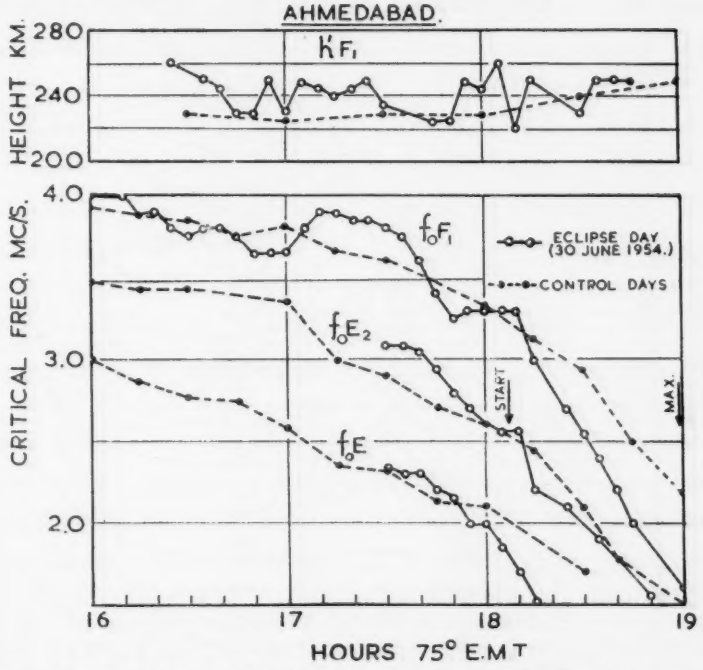


FIG. 1. The variations of $f_0E$, $f_0E_2$, $f_0F_1$ and $h'F_1$ on the control days and on the eclipse days.

An interesting feature was noted in the $F_1$ layer at about 1745 hr. The relevant P'-*f* records are redrawn in Fig. 2 and a few P'-*f*

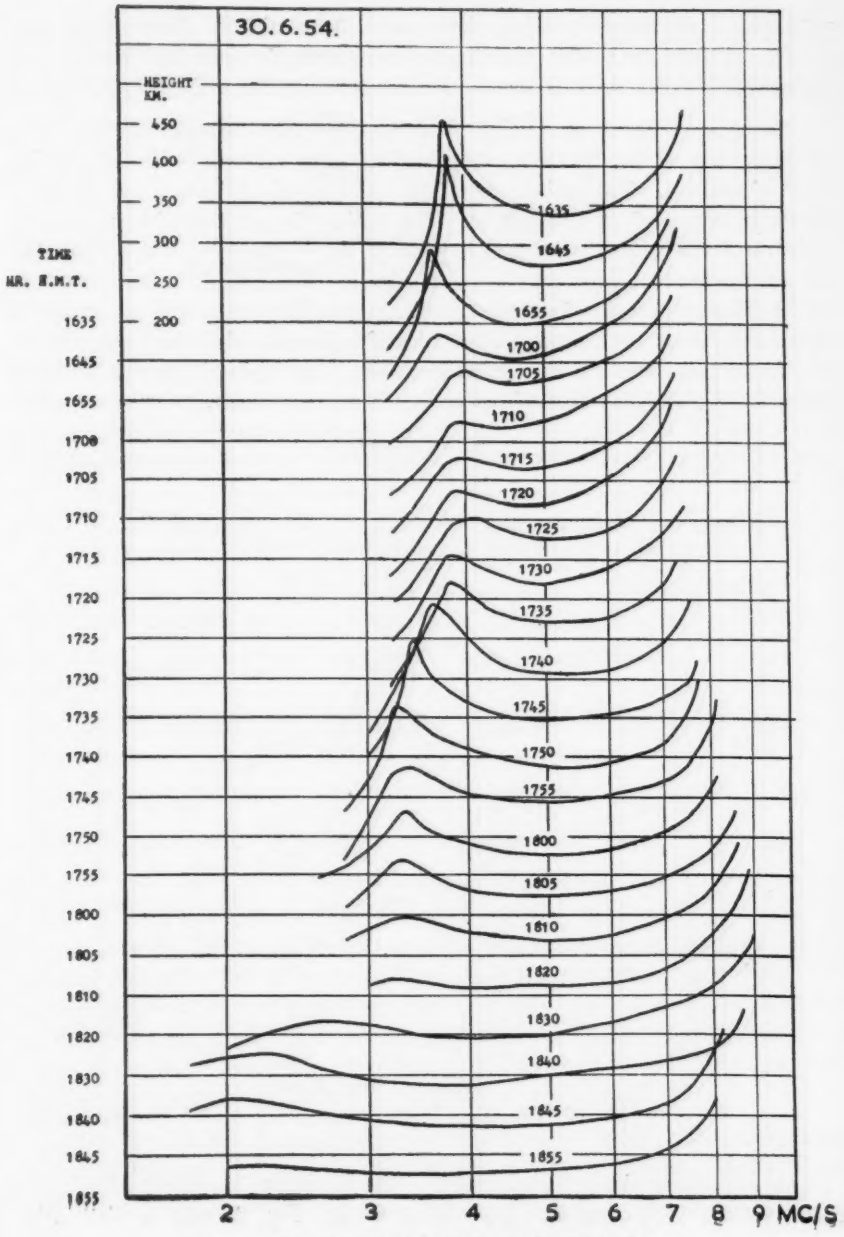


FIG. 2. Few redrawn P'-*f* records on the eclipse day.

records are reproduced in Fig. 3. On normal days with the lowering of the sun, the cusp corresponding to $F_1$ critical frequency gets flatter as the critical frequency decreases, and the identity of the $F_1$ layer gets lost with vanishing inflection on the $F_1$-$F_2$ layer trace. On the 30th June 1954, on the other hand, the $F_1$ layer trace continued to get flatter with the time as on normal days upto about 1720 hr. after which it suddenly increased in sharpness. At 1745 hr. it had a very sharp cusp, and later the cusp died out slowly. During this period, the $F_1$ reflections were very strong and many M reflections were recorded. Curiously, however, the phenomenon occurred about half an hour before the beginning of the eclipse at Ahmedabad.

*$F_2$ layer.*—The variations of the critical frequency ( $f_0F_2$) and the height of maximum ionisation ($h_pF_2$) of the $F_2$ layer on the eclipse day and on the control days are shown in Fig. 4. $f_0F_2$ values were higher on the eclipse day than on the control days. Curiously again, the increase in $f_0F_2$ above the

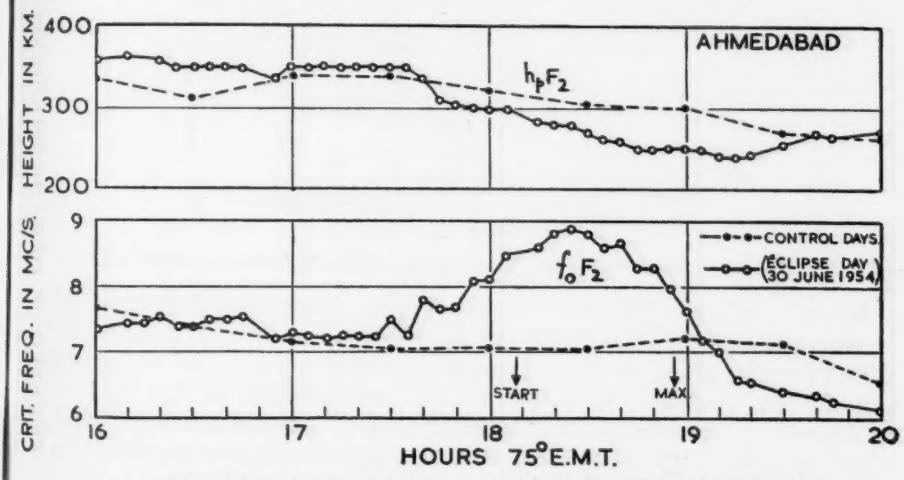


FIG. 4. The variation of $h_pF_2$ and $f_0F_2$ on the control days and on the eclipse day.

normal day values started about half an hour before the beginning of the eclipse. Similar sharp increases of $f_0F_2$ before the start of the eclipse were also noted at some other ionospheric stations, *e.g.*, DeBilt,[1] Tromoya, Kjeller and Tromso,[2] (Landmark *et al.*, 1956) at Slough and Inverness[3] (Minnis, 1956) at Lindau[4] (Becker, 1956). The variations of $f_0F_2$ on a few individual days round the day of the eclipse are shown in Fig. 5. The behaviour on the eclipse day was significantly different from that on normal days.

In order to find how the changes in the critical frequency of the $F_2$ layer were associated with changes in the electron density distribution, the heights of $h_oF_2$, $h_mF_2$ and semi-thickness ($TF_2$) were calculated by Booker and

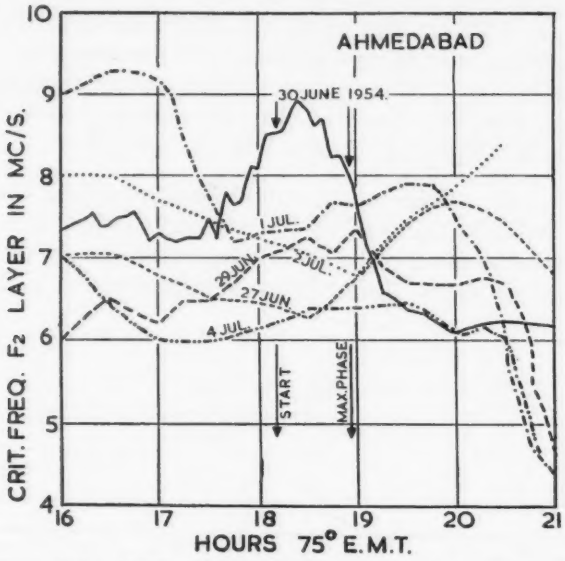


FIG. 5. The variation of $f_oF_2$ on the eclipse day and on the individual control days.

Seaton's method.[5] These are plotted in Fig. 6. The values of the maximum electron density ($N_mF_2$) and total electron content in a vertical column of the $F_2$ layer upto the height of maximum ionisation density ($nF_2$) are also plotted in the same diagram. It is seen that the semi-thickness of the $F_2$ layer increased in the early part of the eclipse period. This increase was mainly due to a lowering of $h_oF_2$. The total electron content therefore showed an increase during the eclipse period.

Another noteworthy change in the $F_2$ reflection traces during the eclipse was the appearance of multiple splitting of the critical frequency and the appearance of range duplication on the first order reflection trace. At 1840 hr., $1\times F_2$ trace became very broad near the end showing a number of critical frequencies, whereas $2\times F_2$ and $3\times F_2$ traces showed clear critical frequencies. A few P′-$f$ records during the period are shown in Fig. 7. At 1845 hr., the broadening of the $F_2$ trace extended to lower frequencies. At 1850 hr., two parallel $F_2$ traces very close to each other were recorded and these were very clear at 1855 hr. The range duplication was observed till 1920 hr.

At 1930, $1\times F_2$ trace was weak and diffused, while $2\times F_2$ was strong and clear, further the critical frequencies of $1\times F_2$ and $2\times F_2$ traces were very different. After 1940 hr. the reflections were again normal. Such abnormal records are not uncommon at Ahmedabad, and these are generally observed later

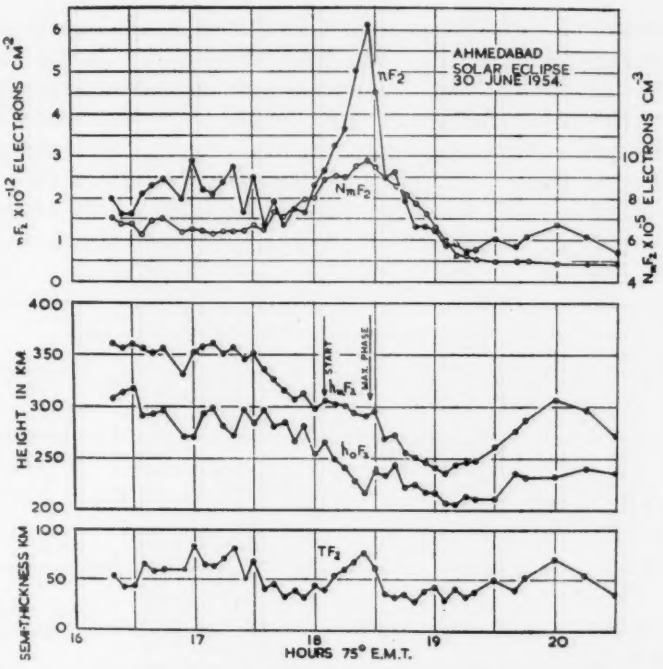


FIG. 6. The variation of $h_mF_2$, $h_oF_2$, $TF_2$, $NmF_2$ and $nF_2$ on the eclipse day.

in the night[6] (Rastogi, 1956). The phenomena can, however, be explained on the basis of a travelling discontinuity or a hump on the surface of the $F_2$ layer. Depending on the position and shape of the discontinuity a particular order of reflections may arrive from different directions and so with slightly differing time delays, and this would give rise to multiple splitting of the critical frequencies and parallel $F_2$ traces. Further, the reflections of a particular order may be selectively focussed by the curved surface of the ionosphere giving rise to anomalous intensity distribution of echoes of different orders[7] (Rastogi, 1956). It may be mentioned that Mitra, S. N.[8] (1955) reported a similar effect in the $F_2$ layer at Delhi round 1905 hr. and described it as triple splitting. Recently, Munro and Heisler[9] (1956) have pointed that if we look at the special situation at any instant during a solar eclipse, then

the resultant distribution of ionisation will be very similar to that caused by a travelling disturbance and would produce anomalies in both $F_2$ and $F_1$ regions. Bramley[10] (1956) has reported that the solar eclipse on 30th June 1954 at Slough, reaching 72% of totality, produced a tilt in the F layer and the direction varied with time as expected from the geometry of the eclipse.

*Sporadic E layer.*—Sporadic ionisations in the E region are more frequent and stronger during summer months at Ahmedabad. During the days of these observations E*s* was abnormally high and often blanketted all the higher reflections extending even above 15 Mc/s. The variations of maximum frequency of E*s* reflections (*f*E*s*) on the eclipse day and on the controlled days are shown in Fig. 8. *f*E*s* increased soon after the start of the eclipse and remained higher than the normal values upto 1900 hr. Very high *f* E*s* can be seen in the P′-*f* records for 1825, 1040 and 1850 hr., reproduced in Fig. 7.

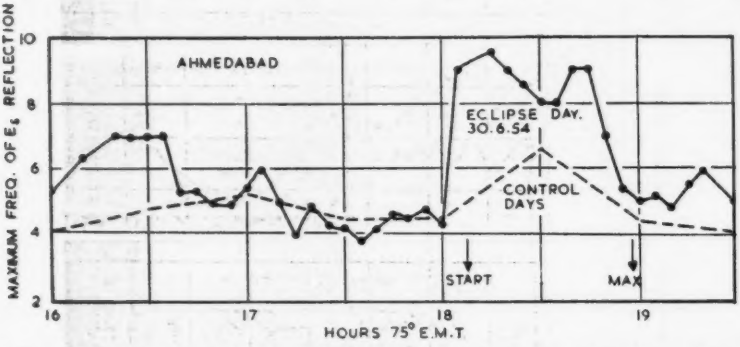


FIG. 8. The variation of maximum frequency of E*s* reflections on the eclipse day and on the control days.

## CONCLUSION

The vertical ionospheric soundings at Ahmedabad during the solar eclipse on 30th June 1954 presented some interesting results. The ionisation of the lower layer E and $F_1$ decreased during the eclipse. Half an hour before the eclipse, the $F_1$ layer showed a sharp cusp with a number of multiple and M reflections. It is difficult to say that this was due to the eclipse. The $F_2$ critical frequencies, as well as the total ion content of the $F_2$ layer during the eclipse, were above normal. The semi-thickness of the $F_2$ layer increased during the eclipse. This was due to a lowering of the base of the $F_2$ layer. It seems that the lower portion of the $F_2$ layer was more affected by the withdrawal of solar radiation than at the level of maximum ionisation. Multiple splitting, range duplication and other effects of the curvature of the ionos-

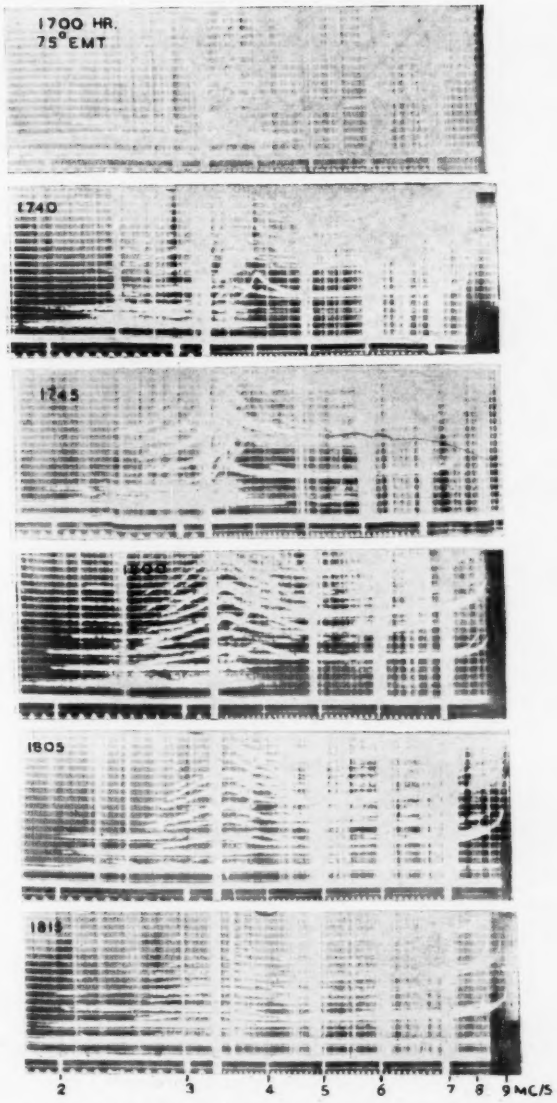


FIG. 3. Few P′′-*f* records showing the sudden sharpening of the $F_1$ cusp and appearance of large number of multiple reflections slightly before the start of the eclipse.

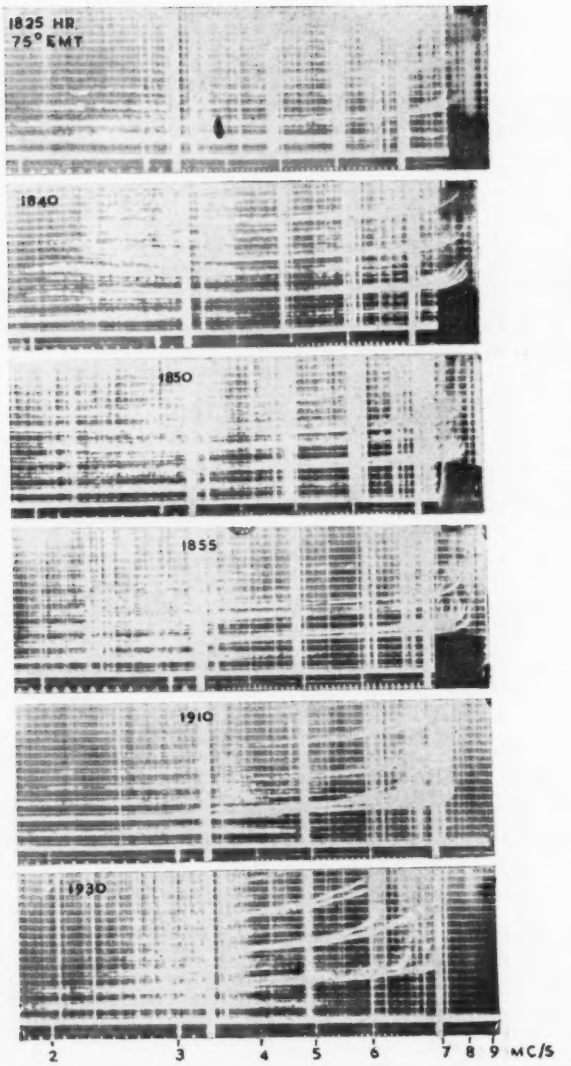


FIG. 7. A few P″-*f* records taken during the eclipse showing range duplication at 1850 to 1920 hr. and anomalous strengthening of 2nd order $F_2$ reflections at 1930.

pheric surface were observed during the eclipse. Maximum E*s* frequencies were higher during the eclipse period.

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# THE 97 Kev. TRANSITION IN THE DECAY OF GADOLINIUM-153

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## Abstract

Decay of $Gd^{153}$ has been studied by means of internal conversion and external conversion data, using Siegbahn-Slätis intermediate image beta-ray spectrometer. The existence of the $96 \pm 2$ Kev. transition in $Gd^{153}$ has been established and its conversion coefficient has been determined.

## Introduction

$Gd^{153}$ has been studied by many workers[1–7] using different techniques and is known to decay by electron capture to $Eu^{153}$. The 102 Kev. transition in this decay is well established. The less intense 70 Kev. transition has been observed and confirmed by previous workers. Another transition proceeding from a level a few Kev. from the 102 Kev. level was reported by McGowan,[7] using the delayed coincidence technique. The existence of this level was confirmed by E. L. Church and Goldhaber,[2] and N. Marty,[4] by means of internal conversion spectrum and an accurate energy of 97·3 Kev. was assigned to this transition by Church and Goldhaber.[2] The previous workers studied the gamma spectrum of this decay by means of scintillation counters. So, a reinvestigation of the gamma spectrum by the external conversion technique using a magnetic spectrometer was considered necessary to obtain more information and to establish clearly the existence of two closely placed transitions at 96 Kev. and 102 Kev.

## Experimental Observations and Results

"Spec-pure" Gadolinium oxide, obtained from Johnson-Matthey and Co., was irradiated in the Harwell pile. Natural Gadolinium contains other isotopes besides $Gd^{152}$. The possible active impurities of Gadolinium are $Gd^{159}$ (18 hr.) and $Gd^{161}$ (3·6 min.). The latter decays to $Tb^{161}$ (7 days). Sufficient time was allowed for these short-lived isotopes to die down. Contribution to the active impurities from other rare-earth isotopes could not be ruled out, but from the spectroscopic analysis of the specimen and on the basis of nuclear data[8] up-to-date, most of the impurity activities were

ruled out from half-life considerations alone, except the long-lived Europium activities. But even the most prominent lines of these Europium isotopes were not observed in our spectra, so that it is inferred that Europium activity in the Gadolinium sample was negligible.

$Gd^{153}$ was studied with the intermediate image beta-ray spectrometer. The internal conversion spectrum clearly indicated the lines which could be identified with $70 \pm 2$ Kev., $102 \pm 2$ Kev. and $96 \pm 2$ Kev. transitions. The ratio of intensity of the K-internal conversion line of $96 \pm 2$ Kev. transition and that due to $102 \pm 2$ Kev. transition was found to be $0{\cdot}20 \pm 0{\cdot}05$ in good agreement with the results of previous workers.

External conversion (photoelectron) spectrum of the electromagnetic radiations from $Gd^{153}$ was studied in the same spectrometer, using a tin converter $0{\cdot}150$ mg./cm.$^2$ thick and nearly $\frac{3}{4}''$ in diameter, deposited by vacuum evaporation on a perspex disc, which was thick enough to absorb the internal conversion electrons from the source. Figure 1 presents part of the photoelectron spectrum. The lower energy part was similar to that[9] obtained

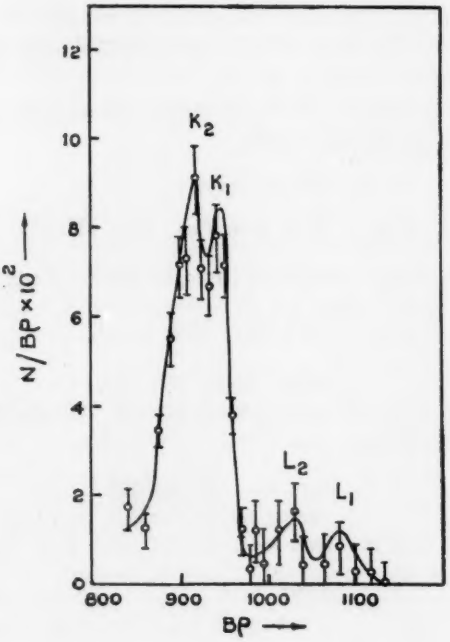


FIG. 1

in the decay of $Sm^{153}$. A photoelectron peak corresponding to $96 \pm 2$ Kev. gamma-ray is seen very close to the peak of the well-known $102 \pm 2$ Kev. gamma-ray. The relative intensity of these neighbouring gamma-rays is estimated from these data to be

$$\frac{I_{\gamma_{96}}}{I_{\gamma_{102}}} = 1 \pm 0{\cdot}1$$

After more than a half-life (235 days) had elapsed, the photoelectron spectrum was observed again. The results of these observations were found to be in agreement with those of the first set.

Knowing the K-internal conversion coefficient of the 102 Kev. transition,[9] the relative intensity of the K-conversion lines of $96 \pm 2$ Kev. transitions and the relative intensity of the corresponding gamma-rays, K-shell internal conversion coefficient of $96 \pm 2$ Kev. was found to be

$$\alpha_{K_{96}} = 0{\cdot}15 \pm 0{\cdot}04$$

When compared with the theoretical value of $\alpha_K$ for 96 Kev. transition from the tables of M.E. Rose,[10] this $96 \pm 2$ Kev. transition is seen to be of E1 type.

Recently, further evidence for the existence of this 96 Kev. transition has been obtained by C. W. Mc Cutchen[11] using scintillation and proportional counters.

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# POLAROGRAPHIC BEHAVIOUR OF METALS IN ETHANOLAMINES

## Part VI. Lead*

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### Introduction

Jessop[1] finds that lead gives a polarographic wave, the top of which is rounded in alkaline triethanolamine solutions. In neutral and alkaline solutions, Gibauld and Faucherre[1a] have derived conclusions on lead-triethanolamine complexes based on the reversibility of the polarographic waves. However, they have not mentioned about the various complicating phenomena that occur when the triethanolamine complexes are reduced at the dropping mercury electrode. Investigations conducted in this laboratory have shown that as in the case of cadmium,[2] nickel,[3] cobalt[4] and copper,[5] lead also gives very good polarographic waves when ethanolamines are used as complexing agents under certain conditions. In the present communication a detailed account of the polarographic behaviour of lead in ethanolamines has been presented.

### Experimental

The details of apparatus and experimental procedure have been described previously.[6] The values of $m$ of the capillaries used have been 1·227 and 1·150 mg. per second and the drop time $t$ has been adjusted to be 5 seconds in normal potassium chloride solution. The polarograms have been recorded at $30° \pm 0·1°$ C.

### Results

1. *Effect of pH.*—The effect of pH on the polarographic behaviour of lead in presence of ethanolamines is given in Table I. The results indicate that the reduction process proceeds reversibly in solutions containing mono- and diethanolamines at all pH values while the reduction process becomes irreversible in highly alkaline solutions when triethanolamine is present.

2. *Effect of variation of the composition of the base electrolyte.*—Preliminary experiments indicated that the tendency for complex formation is

* Part of the Thesis approved for the Degree of Doctor of Science in the University of Mysore.

prominent only in alkaline solutions. Consequently a detailed investigation of the nature of complex formation and wave characteristics has been made in (i) sodium hydroxide, (ii) sodium carbonate and (iii) ammonium chloride-ammonium hydroxide.

(*i*) *Sodium hydroxide.*—In Figs. 1 and 2 are presented polarograms which indicate the effect of di- and triethanolamines in the base solutions.

TABLE I

*Effect of pH on the polarographic behaviour of lead in ethanolamines*

| Amine used | pH | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ (Volt) |
|---|---|---|---|
| Monoethanolamine .. | 6·50 | −0·452 | |
| | | −0·422 | |
| | 9·45 | −0·464 | 0·020 Solution turbid |
| | 11·00 | −0·553 | 0·022 Solution turbid |
| | | −0·514 | |
| | 12·70 | −0·673 | 0·035 |
| | 13·50 | −0·749 | 0·027 |
| Diethanolamine .. | 6·05 | −0·446 | 0·025 |
| | 9·45 | −0·483 | 0·023 Solution turbid |
| | 10·70 | −0·552 | 0·029 |
| | 12·70 | −0·692 | 0·027 |
| | 13·50 | −0·758 | 0·030 |
| Triethanolamine .. | 5·35 | −0·440 | 0·031 |
| | 6·50 | −0·440 | 0·029 |
| | 7·20 | −0·460 | 0·026 |
| | 8·65 | −0·491 | 0·030 |
| | 9·70 | −0·541 | 0·038 |
| | 12·70 | −0·811 | 0·068 |
| | 13·50 | −0·876 | 0·054 |

Curves in monoethanolamine have the same form as those obtained in solutions containing diethanolamine. The curves reveal that the waves are elongated in triethanolamine, while they are quite steep in diethanolamine solutions. The half-wave potentials and the values of $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ of the various reduction waves are given in Table II. While reporting the half-wave potentials or the values of $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ in solutions containing triethanolamine, a correction has been applied for the elongated bend before the diffusion current plateau. Hence these values are somewhat approximate. It is interesting

to note that the waves obtained in solutions containing mono- and diethanolamines are reversible in contrast to the behaviour observed in triethanol-

TABLE II

*Effect of sodium hydroxide on the polarographic behaviour of lead in presence of ethanolamines*

| Amine used | Concentration of | | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ (Volt) | Wave-height s/30 |
|---|---|---|---|---|---|
| | Amine (Molar) | Sodium hydroxide (Molar) | | | |
| * Monoethanolamine | 0·02 | 0·10 | −0·674 | 0·038 | 55·6 |
| | 0·10 | 0·10 | −0·673 | 0·035 | 55·0 |
| | 0·40 | 0·10 | −0·679 | 0·031 | 54·6 |
| | 1·00 | 0·10 | −0·687 | 0·030 | 52·6 |
| | 0·02 | 1·00 | −0·742 | 0·027 | 52·7 |
| | 0·10 | 1·00 | −0·749 | 0·028 | 52·1 |
| | 0·40 | 1·00 | −0·749 | 0·031 | 51·7 |
| | 1·00 | 1·00 | −0·758 | 0·032 | 49·4 |
| * Diethanolamine | 0·02 | 0·10 | −0·675 | 0·028 | 53·2 |
| | 0·10 | 0·10 | −0·692 | 0·027 | 49·0 |
| | 0·40 | 0·10 | −0·711 | 0·031 | 44·9 |
| | 1·00 | 0·10 | −0·725 | 0·032 | 39·7 |
| | 0·02 | 1·00 | −0·750 | 0·027 | 51·5 |
| | 0·10 | 1·00 | −0·758 | 0·030 | 47·2 |
| | 1·00 | 1·00 | −0·789 | 0·032 | 36·3 |
| † Triethanolamine | 0·002 | 0·10 | −0·747 | 0·046 | |
| | 0·02 | 0·10 | −0·758 | 0·063 | |
| | 0·10 | 0·10 | −0·811 | 0·068 | |
| | 0·30 | 0·10 | −0·868 | (Correction for bend) | 44·6 |
| | 0·50 | 0·10 | −0·918 | 0·099 | 43·9 |
| | 0·70 | 0·10 | −0·933 | 0·105 | 43·8 |
| | 1·00 | 0·10 | −0·951 | 0·103 | 42·7 |
| | 0·002 | 1·00 | −0·826 | 0·041 | 42·5 |
| | 0·02 | 1·00 | −0·817 | 0·036 | 43·2 |
| | 0·10 | 1·00 | −0·876 | 0·054 | 41·6 (Correction for bend) |
| | 0·30 | 1·00 | −0·924 | 0·082 | 39·1 |
| | 0·50 | 1·00 | −0·978 | 0·095 | 38·3 |
| | 1·00 | 1·00 | −1·018 | 0·095 | 36·4 |

* Concentration of lead 0·840 millimolar; '*m*' value of capillary 1·150 mg./sec.

† Concentration of lead 1·024 millimolar; '*m*' value of capillary 1·227 mg./sec.

amine solutions where the value of $E_{\frac{1}{4}} - E_{\frac{1}{2}}$ progressively increases with the amine concentration and finally remains constant. Such differences in polarographic behaviour have also been noticed by the present author in the case of cadmium,[2] nickel,[3] cobalt[4] and copper.[5]

(*ii*) *Sodium carbonate.*—The solubility of the complex is very low in solutions containing mono- and diethanolamines to permit polarographic measurements. In Table III the results obtained by employing triethanolamine in the base solution have been presented. It is clear from the results that the reduction is irreversible in character and that the value of $E_{\frac{1}{4}} - E_{\frac{1}{2}}$ attains constancy at higher concentrations of triethanolamine.

TABLE III

*Effect of sodium carbonate on the polarographic behaviour of lead in triethanolamine*

| Concentration of | | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{1}{4}}-E_{\frac{1}{2}}$ (Volt) |
|---|---|---|---|
| Triethanolamine (Molar) | Sodium carbonate (Molar) | | |
| 0·10 | 0·10 | −0·663 | 0·057 |
| 0·50 | 0·10 | −0·762 | 0·073 |
| 1·00 | 0·10 | −0·807 | 0·075 |
| 0·10 | 1·00 | −0·691 | 0·058 |
| 0·50 | 1·00 | −0·773 | 0·072 |
| 1·00 | 1·00 | −0·815 | 0·076 |

(*iii*) *Ammonium chloride-ammonium hydroxide.*—The solubility of the complex increases with an increase in the number of ethanol groups in the amine. In 1·00 M monoethanolamine solutions, there was partial precipitation even with one millimolar lead solutions. The lead was completely soluble in diethanolamine solutions and only a slight precipitation was noticed when the concentration of the amine was reduced to 0·10 M. The waves are well formed in all the amines. The results of analysis of the waves obtained under various conditions are given in Table IV.

TABLE IV

*Effect of ammonium chloride* (1 *M*) *and ammonium hydroxide* (1 *M*) *on the polarographic behaviour of lead in presence of ethanolamines*

| Amine used | Concentration of amine (Molar) | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{1}{2}}-E_{\frac{1}{2}}$ (Volt) |
|---|---|---|---|
| Monoethanolamine .. | 0·10 | −0·441 | 0·027 |
| | 0·50 | −0·500 | 0·032 |
| | 1·00 | −0·536 | 0·033 |
| Diethanolamine .. | 0·10 | −0·509 | 0·026 |
| | 0·50 | −0·537 | 0·032 |
| | 1·00 | −0·548 | 0·032 |
| Triethanolamine .. | 0·02 | −0·510 | 0·032 |
| | 0·50 | −0·553 | 0·030 |
| | 1·00 | −0·565 | 0·032 |

3. *Effect of concentration of lead on diffusion current constant.*—The effect of concentration of lead on the diffusion current constant has not been tried in base solutions containing sodium hydroxide and ethanolamines as the addition of ethanolamines has no practical advantage in the estimation of the metal. However, in sodium carbonate or ammonium chloride-ammonium hydroxide solutions, the presence of ethanolamines makes lead soluble. Due to solubility limitations only one molar triethanolamine is used in presence of sodium carbonate. In ammonium chloride-ammonium hydroxide solutions inclusion of 1·00 M diethanolamine or 0·30 M triethanolamine makes the complex sufficiently soluble to be suitable to polarographic estimation. As a slight maximum appears at higher concentrations of lead in presence of diethanolamine, 0·005% gelatin has been added to the base solution. Table V gives the results obtained. The constancy of the diffusion current constant at different concentrations of lead is quite satisfactory thus rendering the method to be of practical use in the estimation of lead.

## DISCUSSION

1. *Effect of pH.*—The results of the effect of pH on the half-wave potential of lead (Table I) indicate that below pH 7, it is the aquo-lead ion that is getting reduced at the dropping mercury electrode. Between pH 7 and 11 there is complex formation between the amine and the lead ion. Above

TABLE V

*Effect of concentration of lead on the diffusion current constant**

| Concentration of lead (Millimolar) | Diffusion current constant $i_d$ / Cm.$^{\frac{2}{3}}$ $t^{\frac{1}{6}}$ | Concentration of lead (Millimolar) | Diffusion current constant $i_d$ / Cm.$^{\frac{2}{3}}$ $t^{\frac{1}{6}}$ |
|---|---|---|---|
| 1. B.S.: 1·00 M Trien + 0·10 M $Na_2CO_3$ | | 3. B.S.: 1·00 M Dien + ammonium chloride (1 M) + ammonium hydroxide (1 M) + 0·005% gelatin | |
| X = 1·441 at − 1·0 V. *vs.* S.C.E. | | X = 1·450 at − 0·80 V. *vs.* S.C.E. | |
| 0·840 | 3·00 | 0·604 | 3·33 |
| 5·880 | 2·90 | 6·040 | 3·30 |
| 2. B.S.: 1·00 M Trien + 1·00 M $Na_2CO_3$ | | 4. B.S.: 0·30 M Trien + ammonium chloride (1 M) + ammonium hydroxide (1 M). | |
| X = 1·441 at − 1·0 V. *vs.* S.C.E. | | X = 1·450 at − 0·80 V. *vs.* S.C.E. | |
| 0·840 | 2·30 | 0·840 | 3·42 |
| 5·880 | 2·25 | 6·040 | 3·37 |

* *Abbreviations.*—B.S.—Base solution; X—$m^{2/3}t^{1/6}$ in mg.$^{2/3}$ sec.$^{-1/2}$; Dien.—Diethanolamine; Trien.—Triethanolamine.

pH 11, the hydroxyl ion also enters into the complex and there is a steep rise in the half-wave potential.

2. *Splitting of the polarographic wave in triethanolamine.*—In contrast to the behaviour of cadmium,[2] nickel,[3] cobalt[4] and copper[5] splitting of the polarographic wave is practically absent. An elongated bend before the diffusion current plateau has, however, been noticed in solutions containing sodium hydroxide.

3. *Splitting of the polarographic wave in mono- and diethanolamines.*—In these systems even the slight elongated bend observed in triethanolamine is not noticed. The appearance of a small wavelet in monoethanolamine solutions at pH 6·5 is probably due to another species of aquo-lead ion.

4. *Nature of complex formation in sodium hydroxide solutions*: (*i*) *Monoethanolamine.*—The shift in the half-wave potential with an increase in the concentration of the amine is negligible at lower concentrations of the amine (Table II). At higher concentrations however, there is a slight shift in the

half-wave potential indicating complex formation. The following formula can be deduced from the polarographic data as already indicated.[2, 6]

$Pb(Moen)_1(OH)_2$ (between 0·4 M and 1 M monoethanolamine).

(*ii*) *Diethanolamine.*—The data presented in Table II indicate that the stability of the diethanolamine complex is greater than the monoethanolamine complex. From the data of Table II, the following formula has been obtained by the method indicated already.[2, 6]

$Pb(Dien)_1(OH)_2$.

(*iii*) *Triethanolamine.*—In contrast to the behaviour in mono- and diethanolamines, the reduction of the lead complex occurs with varying degrees of reversibility in triethanolamine solutions. However, the extent of irreversibility remains unchanged at concentrations of triethanolamine above 0·5 M. Employing this constant value to calculate $\alpha$[6], it has been found that one triethanolamine group enters into the complex. In this connection it has to be pointed out that whatever may be the degree of irreversibility, the difference in the value of the half-wave potential for 0·1 M and 1·0 M sodium hydroxide is always about 70 mv. It is therefore reasonable to expect that the number of $OH^-$ groups in the complex is two. Hence the formula of the complex can be written as

$Pb(Trien)_1(OH)_2$.

5. *Nature of complex formation in presence of sodium carbonate: Triethanolamine.*—As in the solutions containing sodium hydroxide, the value of $E_{\frac{1}{4}}-E_{\frac{1}{4}}$ becomes constant when the concentration of the amine is above 0·5 M (Table III). The value of $\alpha$ over a concentration range of 0·5–1·0 M triethanolamine is about 0·4, giving 2 for the number of molecules of the amine attached to the complex. Since, under these conditions, there is not much shift in the half-wave potential of lead between 0·1 M and 1·0 M carbonate solutions, it can be concluded that the complex does not have any $CO_3^=$ group associated with it.

6. *Nature of complex formation in presence of ammonium chloride-ammonium hydroxide:* (*i*) *Monoethanolamine.*—The reduction process occurs reversibly in the presence of monoethanolamine as the complexing agent. The shift of the half-wave potential observed with varying concentrations of the amine indicates that at lower concentrations of the amine 3 molecules and at higher concentrations 4 molecules are co-ordinated to the lead ion.

(*ii*) *Diethanolamine.*—The diethanolamine complexes are slightly more stable than the monoethanolamine complexes. As in the case of

monoethanolamine, the reduction proceeds reversibly. From the observed change in the half-wave potential it can be concluded that one molecule of diethanolamine enters into the complex.

(*iii*) *Triethanolamine.*—The reduction of the triethanolamine complex in the base solution containing ammonium chloride-ammonium hydroxide is reversible while in solutions containing either sodium carbonate or hydroxide the wave shows varying degrees of irreversibility. Application of Lingane's equation[2, 6] suggests that one molecule of the amine has entered into the complex.

The results presented in this paper show that ethanolamines form complexes with lead. As in the case of cadmium[2] and copper[5] the reduction process is reversible with mono- and diethanolamines while it is irreversible with triethanolamine, when sodium hydroxide or carbonate are employed in the base solution. This difference is perhaps due to the larger number of hydroxyl groups in triethanolamine which makes the reduction process activation-controlled.

7. *Thermodynamic data from polarographic measurements.*—The dissociation constant, the free energy for the dissociation of the complex and the standard potential for complex formation have been calculated in a manner analogous to that given in a previous communication.[2] The half-wave potential of lead ion at 30° C. in normal potassium nitrate is taken to be $-0{\cdot}409$ V.[7,8] (*vs.* S.C.E.). The standard potential for the reduction reaction $Pb^{++} + 2e = Pb$ at 30° C. has been calculated by the method used by Lingane.[9] The solubility of lead sulphate at 30° C. is taken to be $1{\cdot}6 \times 10^{-4}$ M as given by Kolthoff and Rosenblum.[10] The standard potentials of the two phase lead amalgam–lead sulphate electrode is taken as 0·355 V.[11] (*vs.* N.H.E.) at 30° C. and the potential of the two phase lead amalgam against solid lead is 0·0058 V.[12, 13, 14] (*vs.* N.H.E.). The calculated value for the standard potential of the reduction $Pb^{++} + 2e = Pb$ is $-0{\cdot}130$ V. (*vs.* N.H.E.).

(*i*) *Pb (Moen)$_1$ (OH)$_2$.*—

$$Pb(Moen)_1(OH)_2 \rightarrow Pb^{++} + Moen + 2\,OH^-$$

$K_d = 2{\cdot}45 \times 10^{-12}$: $\Delta F^\circ = +16{\cdot}12$ Kilocals.

$$Pb + Moen + 2\,OH^- \rightarrow Pb(Moen)_1(OH)_2 + 2e;$$

Standard potential $= +0{\cdot}479$ V (*vs.* N.H.E.)

(*ii*) *Pb (Dien)$_1$ (OH)$_2$.*—

$$Pb(Dien)_1(OH)_2 \rightarrow Pb^{++} + Dien + 2\,OH^-$$

$K_d = 2{\cdot}29 \times 10^{-13}$: $\Delta F^\circ = +17{\cdot}55$ Kilocals.

$Pb + Dien + 2\,OH^- \rightarrow Pb(Dien)_1(OH)_2 + 2e$;

Standard potential $= +0{\cdot}510$ V. (*vs.* N.H.E.)

(*iii*) *Pb (Moen)$_4$ (NH$_3$)$_x$ ++.*—

$Pb(Moen)_4(NH_3)_x^{++} \rightarrow Pb^{++} + 4\,Moen + x\,NH_3$

$K_d = 5{\cdot}97 \times 10^{-5}$: $\Delta F° = +5{\cdot}864$ Kilocals.

$Pb + 4\,Moen + x\,NH_3 \rightarrow Pb(Moen)_4(NH_3)_x^{++} + 2e$;

Standard potential $= +0{\cdot}257$ V. (*vs.* N.H.E.)

(*iv*) *Pb (Dien)$_1$ (NH$_3$)$_y$ ++.*—

$Pb(Dien)_1(NH_3)_y^{++} \rightarrow Pb^{++} + Dien + y\,NH_3$

$K_d = 2{\cdot}38 \times 10^{-5}$: $\Delta F° = +6{\cdot}417$ Kilocals.

$Pb + Dien + y\,NH_3 \rightarrow Pb(Dien)_1(NH_3)_y^{++} + 2e$;

Standard potential $= +0{\cdot}269$ V. (*vs.* N.H.E.)

(*v*) *Pb (Trien)$_1$ (NH$_3$)$_z$ ++.*—

$Pb(Trien)_1(NH_3)_z^{++} \rightarrow Pb^{++} + Trien + z\,NH_3$

$K_d = 6{\cdot}49 \times 10^{-6}$: $\Delta F° = +7{\cdot}203$ Kilocals.

$Pb + Trien + z\,NH_3 \rightarrow Pb(Trien)_1(NH_3)_z^{++} + 2e$;

Standard potential $= +0{\cdot}286$ V (*vs.* N.H.E.).

## Summary

1. The polarographic behaviour of lead has been studied at different pH values in presence of sodium hydroxide, sodium carbonate and ammonium chloride-ammonium hydroxide employing the ethanolamines as the complexing agents.

2. The results indicate that the process is substantially reversible in the case of mono- and diethanolamines. In the case of triethanolamine the reduction process shows varying degrees of irreversibility depending upon the concentration of triethanolamine.

3. The formation of the following complexes is indicated by the polarographic data:—

| | | |
|---|---|---|
| $Pb(Moen)_1(OH)_2$ | $Pb(Moen)_3(NH_3)_a^{++}$ | $Pb(Moen)_4(NH_3)_x^{++}$ |
| $Pb(Dien)_2(OH)_2$ | $Pb(Dien)_1(NH_3)_y^{++}$ | $Pb(Trien)_1(OH)_2$ |
| $Pb(Trien)_1(NH_3)_z^{++}$ | $Pb(Trien)_2^{++}$ | |

Moen, Dien and Trien represent monoethanolamine, diethanolamin and triethanolamine respectively.

4. The suitability of employing the reduction waves of lead in ethanolamines for analytical purposes has been discussed.

5. Thermodynamic constants have been calculated from polarographic data in reversible systems.

## ACKNOWLEDGEMENT

The author wishes to express his sincere thanks to Prof. K. R. Krishnaswami and Dr. M. R. A. Rao for their helpful discussions.

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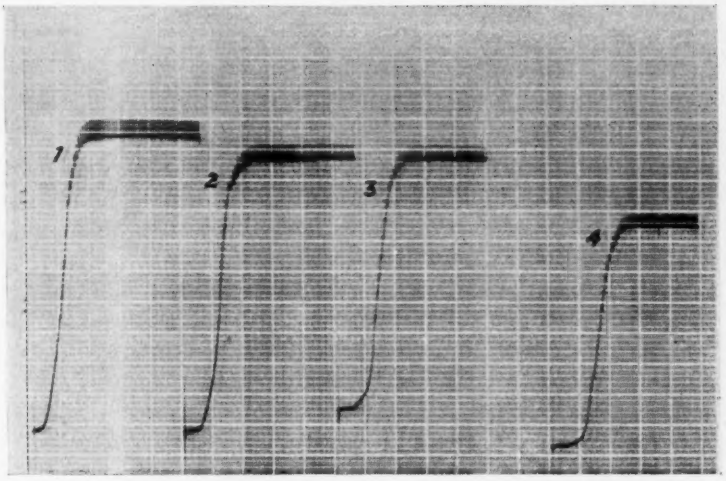


FIG. 1. Effect of sodium hydroxide (0·1 M) on the polarographic behaviour of lead (0·840 millimolar) in diethanolamine.

Curves 1 to 4 have been taken in base solutions containing 0·02, 0·10, 0·40 and 1·00 M diethanolamine respectively. Sensitivity: *s*/30.

The voltage line just preceding eacn polarogram corresponds to − 0·573 V. *vs.* S.C.E.

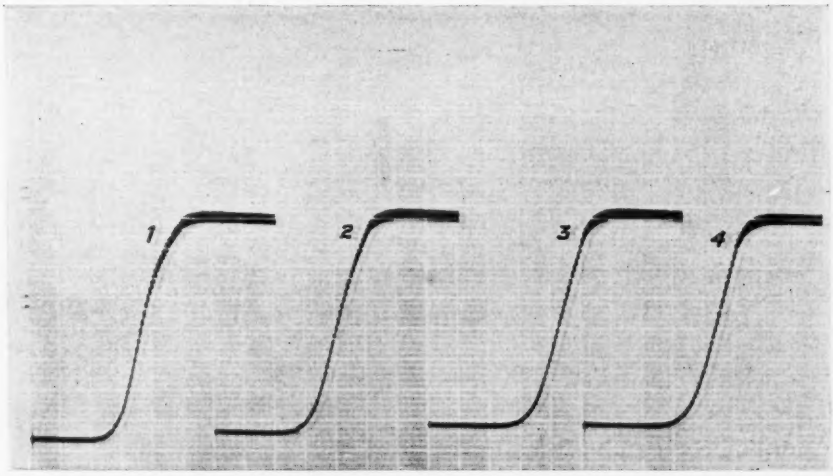


FIG. 2. Effect of sodium hydroxide (1·0 M) on the polarographic behaviour of lead (1·024 millimolar) in triethanolamine.

Curves 1 to 4 have been taken in base solutions containing 0·30, 0·50, 0·70 and 1·00 M triethanolamine respectively. Sensitivity: *s*/30.

The voltage line preceding each polarogram corresponds to − 0·573 V. *vs.* S.C.E

# POLAROGRAPHIC BEHAVIOUR OF METALS IN ETHANOLAMINES

## Part VII. Zinc*

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### Introduction

Jessop[1] has mentioned that the polarographic waves of zinc become poor in shape after incorporating triethanolamine in base solutions containing sodium hydroxide. As has been observed in the case of cadmium,[2] nickel,[3] cobalt,[4] copper[5] and lead,[6] it has been noticed that zinc also gives good polarographic waves in presence of ethanolamines under certain conditions. In the present paper these results have been reported.

### Experimental

The details of apparatus and the experimental procedure have been described previously.[7] The drop time has been 5 seconds in one normal potassium chloride and the value of '$m$' is 1·150 mg. per second. The polarograms have been recorded at 30° ± 0·1° C.

### Results

1. *Effect of pH.*—In Fig. 1 are given some of the polarograms of zinc in di- and triethanolamines at various pH values. The curves obtained by employing monoethanolamine are similar in nature. Table I gives the results of the analysis of the waves.

From the table it is clear that the irreversibility is maximum round about pH 12·7 with all the three ethanolamines. In more alkaline solutions the irreversibility diminishes.

2. *Effect of variation of the composition of the base electrolyte.*—A detailed investigation of the behaviour of zinc-ethanolamine complexes has been made in presence of sodium hydroxide, sodium carbonate and ammonium chloride-ammonium hydroxide and the results obtained are given below.

(i) *Sodium hydroxide.*—Table II indicates the effect of sodium hydroxide on the polarographic behaviour of zinc in the three ethanolamines. It is

* Part of the Thesis approved for the Degree of Doctor of Science in the University of Mysore.

TABLE I

*Effect of pH on the polarographic behaviour of zinc in presence of ethanolamines*

Concentration of amine = 0·1 M. Concentration of zinc = 1·900 millimolar

| Amine used | pH | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{1}{2}} - E_{\frac{1}{4}}$ (Volt) |
|---|---|---|---|
| Monoethanolamine .. | 6·5 | −1·023 | 0·038 |
| | 9·2 | −1·064 | 0·035 |
| | 11·0 | −1·375 | 0·077 |
| | 13·5 | −1·463 | 0·059 |
| Diethanolamine .. | 6·05 | −1·030 | 0·046 |
| | 8·60 | −1·040 | 0·033 |
| | 10·7 | −1·119 | 0·035 |
| | 12·7 | −1·369 | 0·078 |
| | 13·5 | −1·462 | 0·066 |
| Triethanolamine .. | 5·6 | −1·050 | 0·093 |
| | 7·2 | −1·087 | 0·091 |
| | 8·6 | −1·104<br>−1·166 | Elongated bend before diffusion current plateau |
| | 9·7 | −1·154<br>−1·207 | do. |
| | 12·7 | −1·421 | 0·127 |
| | 13·5 | −1·532 | 0·071 |

surprising that the irreversibility is higher in 0·1 M sodium hydroxide than in 1·0 M sodium hydroxide.

(ii) *Sodium carbonate.*—Figure 2 gives some of the polarograms obtained in monoethanolamine. The polarograms in di- and triethanolamines are similar in nature.

It is interesting to note that although zinc carbonate is insoluble in sodium carbonate solutions, yet the complex formed with ethanolamines is sufficiently soluble to enable polarographic measurements. It has been noticed that a slight maximum appears in solutions containing 0·1 M sodium carbonate *plus* monoethanolamine. The maximum, however, disappears on addition of 0·005% gelatin. The results of the polarographic behaviour of zinc-ethanolamine complexes in presence of sodium carbonate are given in Table III.

TABLE II

*Effect of sodium hydroxide on the polarographic behaviour of zinc in ethanolamines*

Concentration of zinc = 1·900 millimolar

| Amine used | Concentration of Amine (Molar) | Concentration of Sodium hydroxide (Molar) | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ (Volt) |
|---|---|---|---|---|
| Monoethanolamine .. | 0·02 | 0·10 | −1·349 | 0·060 |
| | 0·10 | 0·10 | −1·375 | 0·077 |
| | 1·00 | 0·10 | −1·349 | 0·049 |
| | 0·02 | 1·00 | −1·465 | 0·062 |
| | 0·10 | 1·00 | −1·463 | 0·059 |
| | 1·00 | 1·00 | −1·483 | 0·050 |
| Diethanolamine .. | 0·02 | 0·10 | −1·377 | 0·081 |
| | 0·10 | 0·10 | −1·369 | 0·078 |
| | 1·00 | 0·10 | −1·412 | 0·085 |
| | 0·02 | 1·00 | −1·462 | 0·066 |
| | 0·10 | 1·00 | −1·476 | 0·052 |
| | 1·00 | 1·00 | −1·506 | 0·054 |
| Triethanolamine .. | 0·02 | 0·10 | −1·442 | 0·111 |
| | 0·10 | 0·10 | −1·521 | 0·127 |
| | 1·00 | 0·10 | −1·615 | 0·113 |
| | 0·02* | 1·00 | −1·495 | 0·067 |
| | 0·10* | 1·00 | −1·532 | 0·071 |
| | 1·00* | 1·00 | −1·667 | 0·081 |

* The values of half-wave potential and $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ values are approximate due to pressed-in-bend.

From the results presented in Table III it is clear that the reduction process is reversible in monoethanolamine solutions in contrast to the behaviour in di- and triethanolamines.

(iii) *Ammonium chloride* (1 *M*)-*ammonium hydroxide* (1 *M*).—The results of the analysis of the waves are given in Table IV. From the table it is clear that the polarographic waves are reversible in monoethanolamine solutions while in di- and triethanolamines the wave becomes irreversible at higher concentrations of the amine.

TABLE III

*Effect of sodium carbonate on the polarographic behaviour of zinc in ethanolamines*

Concentration of zinc = 1·900 millimolar

| Amine used | Concentration of | | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{3}{4}}-E_{\frac{1}{4}}$ (Volt) |
|---|---|---|---|---|
| | Amine (Molar) | Sodium carbonate (Molar) | | |
| Monoethanolamine .. | 0·10 | 0·10 | −1·215 | 0·050 |
| | 0·50 | 0·10 | −1·251 | 0·042 |
| | 1·00 | 0·10 | −1·268 | 0·032 |
| | 0·10 | 1·00 | −1·274 | 0·038 |
| | 0·50 | 1·00 | −1·294 | 0·027 |
| | 1·00 | 1·00 | −1·310 | 0·024 |
| Diethanolamine .. | 0·10 | 0·10 | −1·190 | 0·047 |
| | 0·50 | 0·10 | −1·177<br>−1·241 | .. |
| | 1·00 | 0·10 | −1·241<br>−1·272 | .. |
| | 0·10 | 1·00 | −1·254 | 0·048 |
| | 0·50 | 1·00 | −1·286 | 0·045 |
| | 1·00 | 1·00 | −1·306 | 0·041 |
| Triethanolamine .. | 0·10 | 0·10 | −1·293 | 0·088 |
| | 0·50 | 0·10 | −1·393 | 0·095 |
| | 1·00 | 0·10 | −1·449 | 0·096 |
| | 0·02 | 1·00 | −1·289 | 0·060 |
| | 0·10 | 1·00 | −1·327 | 0·056 |
| | 0·50 | 1·00 | −1·417 | 0·092 |
| | 1·00 | 1·00 | −1·477 | 0·093 |

3. *Effect of concentration of zinc on the diffusion current constant.*— Table V shows the effect of concentration of zinc on the diffusion current constant in solutions containing sodium carbonate and mono- and triethanolamines. The concentration of the amines have been kept at one molar. The solubility of the complex is greater in mono- than in diethanolamine. Similar behaviour has also been noticed in the case of cadmium.[2] It is surprising that the solubility should be greater in mono- than in triethanolamine. The results indicate that mono- and triethanolamines can be used to estimate zinc polarographically in presence of sodium carbonate. Use of monoethanolamine has a decided advantage over triethanolamine as the waves

TABLE IV

*Effect of ammonium chloride (1 M)-ammonium hydroxide (1 M) on the polarographic behaviour of zinc in presence of ethanolamines*

| Amine used | Concentration of Amine (Molar) | Half-wave potential $E_{\frac{1}{2}}$ *vs.* S.C.E. (Volt) | $E_{\frac{1}{2}}-E_{\frac{1}{2}}$ (Volt) |
|---|---|---|---|
| Monoethanolamine .. | 0·10 | −1·325 | 0·039 |
| | 1·00 | −1·327 | 0·031 |
| Diethanolamine .. | 0·02 | −1·325 | 0·026 |
| | 0·10 | −1·340 | 0·044 |
| | 1·00 | −1·348 | 0·040 |
| Triethanolamine .. | 0·02 | −1·319 | 0·028 |
| | 0·10 | −1·334 | 0·032 |
| | 1·00 | −1·380 | 0·057 |

TABLE V

*Effect of concentration of zinc on the diffusion current constant in presence of sodium carbonate and mono- and triethanolamines*

| Amine used | Concentration of | | $m^{\frac{2}{3}}t^{\frac{1}{6}}$ in mg.$^{2/3}$ sec.$^{-1/2}$ | Diffusion current constant $\frac{i_d}{Cm^{2/3}t^{1/6}}$ |
|---|---|---|---|---|
| | Zinc (Millimolar) | Sodium carbonate (Molar) | | |
| Monoethanolamine* (one molar) | 1·900 | 0·10 | 1·400 at −1·47 V. *vs.* S.C.E. | 3·38 |
| | 19·00 | 0·10 | do. | 3·38 |
| | 1·900 | 1·00 | do. | 2·61 |
| | 19·00 | 1·00 | do. | 2·55 |
| Triethanolamine .. (one molar) | 1·900 | 0·10 | 1·361 at −1·77 V. *vs.* S.C.E. | 2·50 |
| | 9·500 | 0·10 | do. | 2·48 |
| | 1·900 | 1·00 | do. | 1·95 |
| | 9·500 | 1·00 | do. | 1·94 |

* 0·005% gelatin has been incorporated.

with the former are reversible in nature. The effect of concentration of zinc on the diffusion current in presence of ethanolamines and sodium hydroxide

or ammonium chloride-ammonium hydroxide has not been tried as the incorporation of the ethanolamines into base solutions containing sodium hydroxide or ammonium chloride-ammonium hydroxide does not offer any additional advantage. To eliminate the maximum in base solutions containing sodium carbonate and monoethanolamine 0·005% gelatin has been incorporated in the solution.

4. *Dissociation constants of the complexes of cadmium, copper, lead and zinc.*—In Table VI are collected the dissociation constants of complexes as calculated from the polarographic data for mono- or diethanolamine containing the hydroxyl or the carbonate group in addition to the amine.

TABLE VI

*Dissociation constants of metallic complexes*

| Metal used | Formula of the complex | Dissociation constant |
|---|---|---|
| Cadmium[2] .. | $Cd(Moen)_2(OH)_2$ | $2{\cdot}24\times10^{-9}$ |
| | $Cd(Moen)_2(CO_3)_1$ | $1{\cdot}21\times10^{-7}$ |
| | $Cd(Dien)_2(OH)_2$ | $1{\cdot}23\times10^{-9}$ |
| | $Cd(Dien)_2(CO_3)_1$ | $9{\cdot}55\times10^{-9}$ |
| Copper[5] .. | $Cu_2(Moen)_4(OH)_3^+$ | $9{\cdot}33\times10^{-19}$ |
| | $Cu(Dien)_1(OH)_2$ | $6{\cdot}46\times10^{-19}$ |
| Lead[6] .. | $Pb(Moen)_1(OH)_2$ | $2{\cdot}45\times10^{-12}$ |
| | $Pb(Dien)_1(OH)_2$ | $2{\cdot}29\times10^{-13}$ |
| Zinc .. | $Zn(Moen)_2(CO_3)_1$ | $1{\cdot}67\times10^{-10}$ |

5. *Wave forms observed in the polarographic reduction of metallic complexes.*—Figure 3 gives a schematic representation of the more important types of polarographic waves that have been observed by the present author in the study of metallic complexes.

## DISCUSSION

1. *Effect of pH.*—The effect of pH on the shift in the half-wave potential (Table I) indicates that below pH 9 there is very little tendency for complex formation and the half-wave potential corresponds very nearly to that of aquo-zinc ion ($E_{\frac{1}{2}}$ of aquo-zinc ion ca. $-1{\cdot}00$ V *vs.* S.C.E.). As the pH is increased beyond 9 there is the formation of the amine complex and when

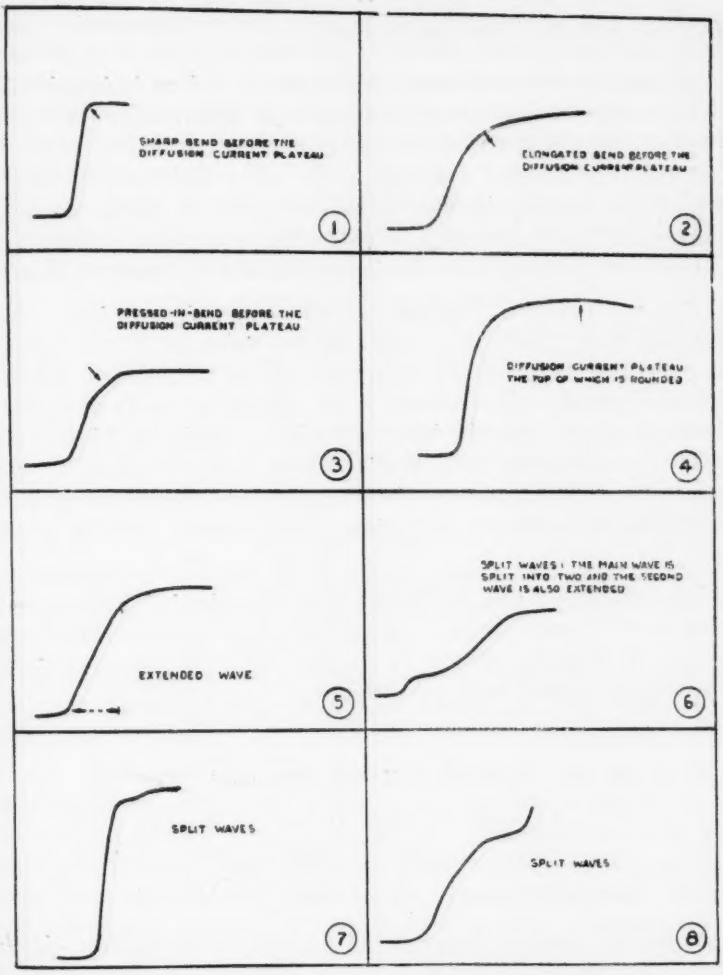


FIG. 3. Schematic Representation of Some Polarographic Wave Types.

the pH reaches 12 there is a further entry of the hydroxyl groups into the complex and there is a steep rise in the half-wave potential.

2. *Splitting of the polarographic wave in triethanolamine.*—Waves of zinc-triethanolamine complexes show very little tendency for splitting. The elongated bend that appears at pH 8·6 and 9·7 is probably due to another amine complex in sluggish equilibrium.[2]

3. *Splitting of the polarographic wave in mono- and diethanolamines.*—In these solutions splitting is practically absent.

4. *Nature of complex formation in presence of sodium hydroxide.*—That ethanolamines have entered into the complex is obvious from the shift in the half-wave potential when the concentration of the amine is changed from 0·1 M to 1·0 M and from the change in the irreversibility of the electrode process when the concentration of the amine in the base solution is altered. The slight change in the half-wave potential with the amine is evidently due to the similar stabilities of the hydroxyl and the amine complexes of zinc.

5. *Nature of complex formation in presence of sodium carbonate.*—Employing equations for reversible[2] and irreversible[7] processes, it has been found that two molecules of the amine have entered into the complex. It is difficult to compute the number of carbonate groups that enter the complex due to the wide degree of irreversibility in di- and triethanolamine solutions. However, in monoethanolamine solutions, it can be said that one $CO_3^=$ group is present in the complex as the reduction proceeds quite reversibly in 1 M monoethanolamine solutions containing 0·10 M and 1·00 M sodium carbonate.

Taking a value − 1·016 V. (*vs.* S.C.E.)[8,9] for the half-wave potential of zinc ion at 30° C. and − 0·762 V. (*vs.* N.H.E.)[10] at 30° C. for the standard potential of the reduction process $Zn^{++} + 2e = Zn$, the following thermodynamical constants have been calculated.

(i) *Zn (Moen)$_2$ (CO$_3$)$_1$.*—

$$Zn\,(Moen)_2\,(CO_3)_1 \rightarrow Zn^{++} + 2\ Moen + CO_3^=$$

$K_d = 1{\cdot}67 \times 10^{-10}$: $\Delta F^\circ = +\ 13{\cdot}57$ Kilocals.

$$Zn + 2\ Moen + CO_3^= \rightarrow Zn\,(Moen)_2\,(CO_3)_1 + 2e;$$

Standard potential = + 1·056 V (*vs.* N.H.E.).

6. *Nature of complex formation in presence of ammonium chloride-ammonium hydroxide.*—In presence of ammonium chloride and ammonium hydroxide the shift in the half-wave potentials by the variation of the concentration of the amine is very small. The entry of ethanolamines into the complex is, however, obvious from the fact that the reversibility of the reduction process is affected by changing the concentration of the amines (Table IV). The closeness of the half-wave potentials of the ammonia complex ($E_{\frac{1}{2}} = -\ 1{\cdot}33$ V. *vs.* S.C.E.) and ethanolamino-ammonia complexes indicates that the stabilities of the complexes are very nearly the same.

7. *Irreversibility of the polarographic waves.*—The polarographic waves of the ethanolamine complexes are mostly irreversible. The reduction process is reversible only in solutions containing monoethanolamine and sodium carbonate. As has been noticed previously by the present author in nickel[3] and cobalt[4] complexes, the irreversibility increases with the number of ethanol groups in the amine.

In conclusion it can be stated that the ethanolamines enter the hydroxy and ammonia complexes of zinc. It has not been possible to find out the number of groups of ethanolamines that enter the complex, as the stability of the complexes with and without ethanolamines happens to be of the same order. However, it can be stated that two molecules of the ethanolamines enter the complex in sodium carbonate solutions.

8. *Comparative stability of the complexes of cadmium, copper, lead and zinc.*—Mellor and Maley[11] have stated that the stability of the complexes of bivalent metal ions follows the following order irrespective of the nature of the ligand involved.

$$Pd > Cu > Ni > Pb > Co > Zn > Cd > Fe > Mn > Mg$$

The results presented in Table VI indicate that similar order is followed even in the case of like complexes which contain two different types of ligands in the complex.

9. *Wave forms observed in the study of metallic complexes.*—The more important wave forms that have been noticed in the work on metallic complexes[2–6, 12] (Fig. 3) can be classified thus:—

(i) Waves with a sharp, elongated or pressed-in bend before the diffusion current plateau, (ii) waves whose diffusion current plateau is rounded, (iii) split waves and (iv) extended waves. Polarographic waves with elongated or pressed-in bend before the diffusion current plateau and the split waves are due to sluggish equilibrium between two species of complexes both the species being reduced to the same state. Extended waves indicate the irreversibility of the electrode process and with such waves the value of $E_{\frac{1}{4}} - E_{\frac{1}{4}}$ are more than the values for reversible polarographic waves.

10. *Theory of irreversible polarographic waves employed to derive conclusions regarding the formulæ of metallic complexes.*—It has to be pointed out that the irreversible wave equations[7, 13] employed have certain limitations. The equation for the C-V curve contains a constant '*s*' which depends on the nature of the electrode. If '*s*' changes then the rate of irreversible electron transfer also changes. It is assumed that '*s*' will not alter when the concentration of the ligand is changed. In the treatment of the

irreversible waves the final equation is usually obtained by neglecting the reverse reaction. Goto and Tachi[14] have indicated that the electrode process can be regarded as fully irreversible when the value of $\alpha < 0{\cdot}5$, corresponding to a value of $E_{\frac{1}{4}} - E_{\frac{1}{2}} > 0{\cdot}057$ V., for a two-electron reduction process. However, the results recorded in the present series of investigations[2-7, 15] indicate that, when equations of similar form can be applied to reversible and also to fully irreversible processes, very reasonable conclusions can be drawn even in the case of partially irreversible processes, in the case of metal ion discharge. In the case of metallic complexes getting reduced from one oxidation state to another, $(p - q)$ appears in the equation for reversible reduction[7] while only '$p$' appears in the equation for fully irreversible reduction. Unfortunately, in the present work, not many such electrode processes of varying degrees of irreversibility have been met with. The value of $\alpha$ for the irreversible reduction of $Fe^{+++} \rightarrow Fe^{++}$ in 0·1 M triethanolamine solution and 0·1 or 1·0 M sodium carbonate[7] is about 0·85. It has been concluded that the irreversibility of the first iron wave is not sufficiently high to warrant the elimination of '$q$' in $(p - q)$. However, in pyrophosphate solutions[12] the slope of the log plot for the same reduction step is 0·18 V., indicating that the reduction process is fully irreversible. In this case conclusion regarding the formula of the ferric complex has been drawn by applying the equations of the irreversible waves. The irreversible wave equation has to be applied only when the polarographic wave is completely irreversible, as it is very difficult to imagine how '$q$' can disappear in the case of a reduction wave of slight irreversibility. The theoretical treatment of irreversible processes is still undeveloped to be of general applicability.

## SUMMARY

1. The polarographic behaviour of the ethanolamine complexes of zinc has been studied at various pH values and in the presence of sodium hydroxide, sodium carbonate and ammonium chloride-ammonium hydroxide.

2. The reduction process is essentially irreversible, the degree of irreversibility increasing with the number of ethanol groups in the amine.

3. It has not been possible to elucidate from polarographic data the number of ethanolamine groups that enter the complex in solutions containing sodium hydroxide or ammonium chloride-ammonium hydroxide due to the closeness in the stability of the various complexes.

4. The following complexes have been indicated from the polarographic data:—

$Zn(Moen)_2(CO_3)_1$ $Zn(Dien)_2(CO_3)_x^{2-2x}$ $Zn(Trien)_2(CO_3)_y^{2-2y}$

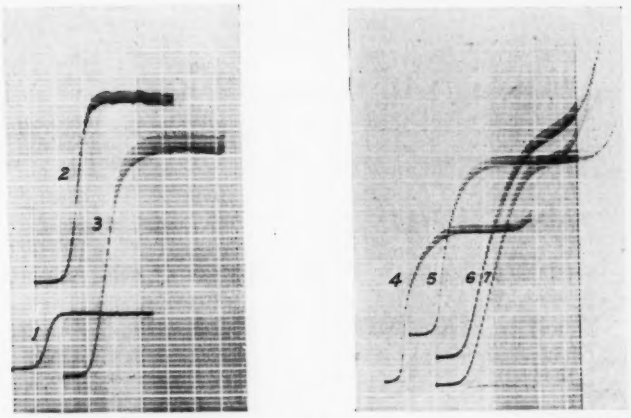


FIG. 1. Effect of pH on the polarographic behaviour of zinc (1·900 millimolar) in di- and triethanolamines.

Curves 1 to 3 have been taken in diethanolamine solutions at pH 10·70, 8·60, and 6·05 at *s*/15, *s*/30 and *s*/70 respectively. There was partial precipitation at pH 10·70 and 8·60.

Curves 4 to 7 have been taken in triethanolamine solutions at pH 9·70, 8·65, 7·20 and 5·60 at *s*/70 respectively. There was partial precipitation at pH 9·70 and 8·65.

The voltage lines just preceding the polarograms correspond to − 0·973, − 0·873, − 0·873, − 1·073, − 0·973, −0·873 and − 0·873 V. *vs.* S.C.E. respectively.

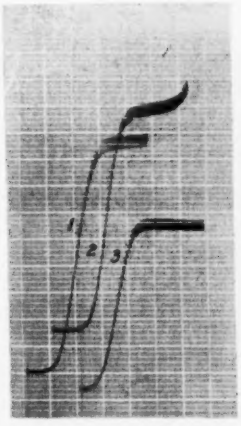


FIG. 2. Effect of sodium carbonate (0·1 M) on the polarographic behaviour of zinc (1·900 millimolar) in monoethanolamine.

Curves 1 to 3 have been taken in base solutions containing 0·005% gelatin and 0·50, 1·00 and 0·10 M monoethanolamine respectively.

There was slight precipitation in 0·1 M monoethanolamine solution.

Sensitivity: *s*/70.

The voltage line just preceding each polarogram corresponds to − 1·073 V. *vs.* S.C.E.

Moen, Dien, and Trien represent monoethanolamine, diethanolamine and triethanolamine respectively.

5. The reduction waves of zinc-ethanolamine complexes can be used for the estimation of zinc in sodium carbonate solutions.

6. Thermodynamic constants are calculated from polarographic data in the case of the reversible system.

7. Some important types of polarographic wave forms obtained in the study of metallic complexes have been given.

8. The limitations regarding the use of irreversible wave equations to derive the formulæ of metallic complexes have been pointed out.

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# INVESTIGATIONS IN NON-AQUEOUS SOLVENTS

## Part III.[1] Solubility and Conductances of Some Metal Nitrites in Ethylenediamine and Monoethanolamine

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### INTRODUCTION

THIS investigation represents a part of a programme being carried out in this laboratory, concerned with the conductance of and electrodeposition in non-aqueous solutions. The importance of experiments with basic solvents has been outlined in an earlier paper,[1] in which the conductance behaviour of some rare earth metal acetates in ethylenediamine was presented. The objective of the investigation reported here is to determine the solubility and conductances of nitrites of sodium, potassium and silver in anhydrous ethylenediamine and monoethanolamine. It has been found that salts containing anions of the type $[XO_2]^-$ are soluble in ethylene glycol owing to hydrogen bonding.[2] Since there is a close analogy between $(OH)^-$ and $(NH_2)^-$ groups according to the Franklin concept and since ethylenediamine and monoethanolamine are capable of hydrogen bond formation with $[XO_2]^-$ type anions, the investigation of the solubility and electrolytic behaviour of some univalent metal nitrites in the solvents mentioned above was undertaken. Some important physical constants of the two solvents are given in Table I.

TABLE I

*Physical constants of solvents at* 25° *C.*

| Compound | B.P. ° C. | Density g./ml. | Ionization constant | Dielectric constant | Viscosity millipoises |
|---|---|---|---|---|---|
| Ethylenediamine | 116·2 | 0·891 | $8·5\times10^{-5}$ | 12·9 | 15·4 |
| Monoethanol-amine | 171·1 | 1·0117 | $2·77\times10^{-5}$ | 37·72 | 193·5 |

### EXPERIMENTAL

1. *Purification of solvents.*—Pure anhydrous ethylenediamine was obtained from commercial ethylenediamine monohydrate (B.D.H.) as pre-

viously outlined. Monoethanolamine was purified by the procedure of Isbin and Kobe. The product boiled at 171° and had a specific conductivity of $3 \cdot 21 \times 10^{-5}$ mho/cm. at 30° C. The ethylenediamine had a specific conductivity of $2 \cdot 16 \times 10^{-6}$ mho/cm. at 30° C.

2. *Preparation of anhydrous metal nitrites.*—Analytically pure sodium nitrite and potassium nitrite were powdered and dried at 200° for several hours and preserved in desiccators containing phosphorus pentoxide. Silver nitrite was prepared by mixing solutions of pure silver nitrate and sodium nitrite. The precipitated silver nitrite was washed thoroughly with ice-water, then with 95% ethanol, dried in air in a dish protected from sunlight for one day, and finally over anhydrous calcium chloride at reduced pressure for two days and stored in a brown bottle protected from light.[3]

3. *Apparatus and manipulation.*—All the metal nitrites, anhydrous solvents and solutions were handled in a Dry Box as outlined in an earlier paper.[1]

4. *Solubility determinations.*—The respective powdered metal nitrite was added in small amounts slowly and with brisk shaking to about 20 ml. of the anhydrous solvent in a big test-tube fitted with a ground-glass stopper until some of the solute remained undissolved. Then the contents in the stoppered tubes were thermostated at $30 \pm 0 \cdot 05°$ C. for a sufficiently long period with frequent agitation. Afterwards, the tube was centrifuged for twenty minutes and opened inside the Dry Box. Silver nitrite was the only one among the three salts, which dissolved in both ethylenediamine and monoethanolamine with evolution of heat, giving brownish black solutions. Sodium nitrite solution in ethylenediamine has a pale yellow tinge, while potassium nitrite solutions are colourless. Sodium and potassium contents were estimated by oxidising the organic matter with fuming sulphuric acid and 30% hydrogen peroxide; then the salts were ignited and weighed as sulphates. Silver was estimated gravimetrically as AgCl.

5. *Solvate formation of silver nitrite with ethylenediamine.*—When a saturated solution of silver nitrite in ethylenediamine was allowed to stand for sometime, a colourless, crystalline solvate was obtained. The solvate was pressed between folds of filter-paper inside the Dry Box to remove the excess solvent and then dried in a vacuum desiccator. Later, an analysis of the solvate was made by titrating a weighed quantity dissolved in water against standard N/5 nitric acid to the methyl orange end-point. The silver content of this solution was estimated as silver chloride gravimetrically.

*Anal.*—Calcd. for $AgNO_2 \cdot 2.[C_2H_4(NH_2)_2]$: Ag, 39·37%; $C_2H_4(NH_2)_2$, 43·84%. ; Found: Ag 39·16%; $C_2H_4(NH_2)_2$ 43·11%.

Silver nitrite thus forms a solvate with the formula $AgNO_2.2[C_2H_4(NH_2)_2]$. This type of solvate formation in ethylenediamine has been reported by Isbin and Kobe for these salts.[4] LiCl.2 en, LiBr.2 en, LiI.3 en, NaI.3 en, $NaClO_4$.3 en, $SrCl_2$.6 en, where en = $C_2H_4(NH_2)_2$. Silver nitrite has also been reported to form ammonates like $AgNO_2.n\ NH_3$ where n = 1, 2, and 3.[6] Even with monoethanolamine, silver nitrite gives a white deposit, when a concentrated (almost saturated) solution is allowed to stand for a long time. The white deposit is presumably a solvate of silver nitrite, which undergoes partial decomposition in the presence of traces of moisture, to shining metallic silver. This solvate was not further analysed. The extreme solubility of silver nitrite in the two solvents are due to the solid phase being a solvate in each case.

6. *Conductance measurements.*—Conductances of the various solutions were obtained after thermostating at 30° ± 0·05° C. at definite dilutions as previously outlined[1]. The cell constant of the cell employed was 0·1991 $cm.^{-1}$ The specific conductivity of the solvent was subtracted from that of the solution in each case.

## RESULTS AND DISCUSSION

*Solubility determinations.*—The solubilities of sodium, potassium and silver nitrites in ethylenediamine and monoethanolamine are summarised in Table II along with solubilities in liquid ammonia and water reported in literature. In addition, comparisons with available literature values for corresponding nitrates in the above-mentioned solvents, have also been made.

TABLE II

*Solubility data of some metal nitrites and nitrates in various solvents*

| Salt | Solubility expressed in g. of salt/100 g. of solvent | | | |
|---|---|---|---|---|
| | Ethylene-diamine | Monoethanol-amine | Ammonia[5] | Water |
| $NaNO_2$ .. | 12·60[t1] | 8·74[t1] | *v.s.* | 84[t3] |
| $KNO_2$ .. | 3·86[t1] | 4·52[t1] | *v.s.* | 302[t3] |
| $AgNO_2$ .. | 52·36[t1] | 70·53[t1] | *v.s.* | 0·5[t4] |
| $NaNO_3$ .. | 33·5[t2] | .. | 97·6[t2] | 91·5[t2] |
| $KNO_3$ .. | 0·37[t2] | .. | 10·4[t2] | 37·9[t2] |
| $AgNO_3$ .. | .. | .. | 86·04[t2] | 73·5[t1] |

($t_1$ = 30° C.; $t_2$ = 25° C.; $t_3$ = 20° C.; $t_4$ = 18° C.; *v.s.* = very soluble.)

The order of solubility of nitrites in ethylenediamine and monoethanolamine is similar. The solubility trend of nitrates in ammonia and water resembles that of nitrites in ethylenediamine and monoethanolamine. The solubility increases from potassium to silver through sodium in all cases except in the case of these nitrites in water. The much lower solubility of potassium nitrite in comparison with that of sodium nitrite in both the basic solvents can be attributed to the poorer tendency of $K^+$ ion to associate with basic solvents.[8] The very high solubility of silver nitrite and its solvate formation in the two basic solvents in comparison with the solubilities of the alkali nitrites, is due to the acidic nature of the $Ag^+$ ion[8] and also due to the structural differences between silver and alkali nitrites[12]. Sodium nitrite dissolves less in monoethanolamine than in ethylenediamine, while potassium and silver nitrites have greater solubilities in the former solvent. Most of the salts so far examined are more soluble in monoethanolamine than in ethylenediamine, but instances where sodium salts dissolve less in the former than in the latter, can also be noticed in the earlier literature.[4]

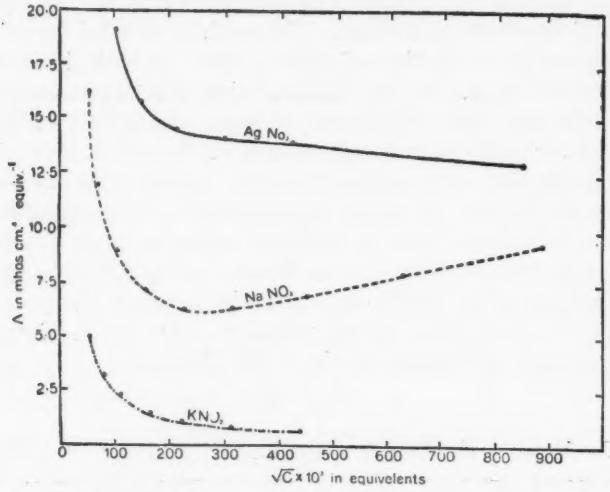
TABLE III

*Conductance data for ethylenediamine solutions at* 30° *C.*

| $NaNO_2$ | | | $KNO_2$ | | | $AgNO_2$ | | |
|---|---|---|---|---|---|---|---|---|
| Concn., C., equiv./litre | $\sqrt{C}\times10^3$ | $\Lambda$ | Concn., C., equiv./litre | $\sqrt{C}\times10^3$ | $\Lambda$ | Concn., C., equiv./litre | $\sqrt{C}\times10^3$ | $\Lambda$ |
| 0·7962 | 892 | 9·258 | .. | .. | .. | 0·7292 | 854 | 12·87 |
| 0·3981 | 630 | 7·932 | .. | .. | .. | 0·3646 | 604 | 13·48 |
| 0·1990 | 446 | 6·889 | 0·1940 | 440 | 0·722 | 0·1823 | 427 | 13·99 |
| 0·0995 | 315 | 6·433 | 0·0970 | 312 | 0·890 | 0·0912 | 302 | 14·06 |
| 0·0498 | 223 | 6·510 | 0·0485 | 220 | 1·154 | 0·0456 | 214 | 14·51 |
| 0·0249 | 158 | 7·190 | 0·0243 | 156 | 1·576 | 0·0228 | 151 | 15·78 |
| 0·0124 | 111 | 9·033 | 0·0122 | 110 | 2·273 | 0·0114 | 107 | 19·00 |
| 0·0062 | 79 | 11·93 | 0·0061 | 78 | 3·248 | 0·0057 | 76 | 22·83 |
| 0·0031 | 56 | 16·23 | 0·0030 | 55 | 5·034 | .. | .. | .. |
| 0·0016 | 40 | 20·19 | .. | .. | .. | .. | .. | .. |

*Conductance studies.*—Typical conductance data in anhydrous ethylenediamine and anhydrous monoethanolamine (equivalent conductance, $\Lambda$ mhos. cm.$^2$ equiv.$^{-1}$ and concentration of the salt in gram equivalents per litre, C)

as summarised in Tables III and IV and Figures 1 and 2 respectively, indicate that the nitrites are more conducting in anhydrous ethylenediamine than in anhydrous monoethanolamine.



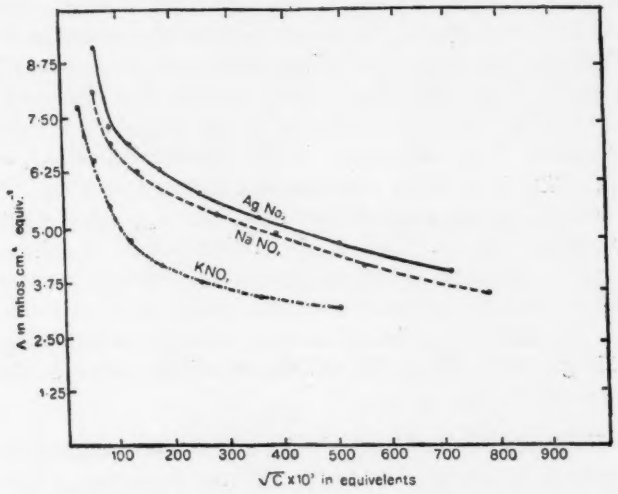

TEXT-FIG. 1. Conductances of Nitrites of Na, K and Ag in Anhydrous Ethylenediamine at 30° C.

TABLE IV

*Conductance data for monoethanolamine solutions at* 30° *C.*

| $NaNO_2$ | | | $KNO_2$ | | | $AgNO_2$ | | |
|---|---|---|---|---|---|---|---|---|
| Concn., C., equiv./litre | $\sqrt{C}\times10^3$ | Λ | Concn., C., equiv./litre | $\sqrt{C}\times10^3$ | Λ | Concn., C., equiv./litre | $\sqrt{C}\times10^3$ | Λ |
| 0·6150 | 784 | 3·424 | 0·2594 | 509 | 3·074 | 0·5120 | 716 | 3·986 |
| 0·3075 | 555 | 4·212 | 0·1297 | 360 | 3·321 | 0·2560 | 506 | 4·586 |
| 0·1538 | 392 | 4·871 | 0·0648 | 255 | 3·771 | 0·1280 | 358 | 5·207 |
| 0·0769 | 277 | 5·335 | 0·0324 | 180 | 4·132 | 0·0640 | 253 | 5·782 |
| 0·0384 | 196 | 5·811 | 0·0162 | 127 | 4·660 | 0·0320 | 179 | 6·320 |
| 0·0192 | 139 | 6·302 | 0·0081 | 90 | 5·494 | 0·0160 | 127 | 6·881 |
| 0·0096 | 98 | 6·916 | 0·0040 | 63 | 6·613 | 0·0080 | 89 | 7·300 |
| 0·0048 | 69 | 8·127 | 0·0020 | 45 | 7·100 | 0·0040 | 63 | 9·125 |
| .. | .. | .. | 0·0010 | 32 | 7·700 | .. | .. | .. |

Among the three nitrites investigated, potassium nitrite is the least conducting in both the solvents. The marked increases in equivalent conductances with increasing dilution in both the solvents are apparent except in the case of the ethylenediamine solution of sodium nitrite. In the latter case a conductance minimum is obtained at a concentration of 0·0676 gm. equiv./litre.




TEXT-FIG. 2. Conductance of Nitrites of Na, K and Ag in Anhydrous Monoethanolamine at 30° C.

Comparisons of conductance data for metal nitrites in ethylenediamine and monoethanolamine are of interest. Monoethanolamine has a higher dielectric constant and viscosity than ethylenediamine (Table I). Since inherently ionic compounds are considerably ionised in these solvents, the governing factor here is viscosity rather than dielectric constant. The higher viscosity of monoethanolamine reduces the ionic mobilities to a considerable extent, resulting in the lowering of the equivalent conductances. The observed lower equivalent conductances of these inherently ionic metal nitrites in monoethanolamine than in ethylenediamine are thus in accord with this view of Moeller and Zimmermann[7]; potassium nitrite seems to be an exception to this view. On the other hand, with inherently covalent compounds like the metal acetates, dielectric constant seems to be prominent in making them more conducting in monoethanolamine than in ethylenediamine, owing to the higher dielectric constant of the former than the latter.[7]

The greater conductivity of silver nitrite than that of sodium nitrite in both the solvents studied, parallels the conductance behaviour of silver and sodium nitrates in ethylenediamine.[9] The lower conductivity of potassium nitrite in comparison with that of sodium nitrite in both the solvents parallels the conductance behaviour of potassium and sodium bromides in liquid ammonia.[11]

It has been mentioned earlier in this paper, that sodium nitrite among the three nitrites investigated, shows an equivalent conductance minimum in ethylenediamine but not in monoethanolamine (see Figs. 1 and 2). Occasionally in media of low dielectric constant a minimum in equivalent conductance is encountered. The concentration at that minimum is related to the dielectric constant, D, of the solvent by the relationship $D^3/c_{min} = \text{constant}$ (P. Walden, 1922) for a given electrolyte in different solvents. So, as the dielectric constant of the medium increases, the $c_{min}$ also shifts towards more concentrated regions. The $c_{min}$ for sodium nitrite in ethylenediamine is 0·0676 gm. equiv./litre. Applying the above Walden's relationship, the $c_{min}$ for sodium nitrite in monoethanolamine should occur at about 1·69 gm. equiv./litre. As this exceeds the solubility of sodium nitrite in monoethanolamine (1·284 gm. equiv./litre) the occurrence of the same in this solvent becomes improbable.

R. M. Fuoss and C. A. Kraus who have extensively studied the conductance behaviour of tetraisoamyl ammonium nitrate in media of low dielectric constant employing water-dioxane mixtures were able to explain the conductance minimum encountered and prove the validity of Walden's rule on the basis of ion-pair, and ion-triplet formation.[10] These authors showed that as the concentration of the electrolyte increases, the extent of ion-association to form pairs, *viz.*, $+\ -$ will increase, resulting in the lowering of equivalent conductances. With increasing concentration of the electrolyte, however, triple ions, *viz.*, $+\ -\ +$ and $-\ +\ -$, will commence to form but as these have a resultant charge the equivalent conductance tends to rise again.[10] The above mode of explanation appears to explain the conductance minimum encountered in the case of sodium nitrite in ethylenediamine which has a low dielectric constant (12·9 at 25° C.). It has also been shown that in solvents of dielectric constant exceeding 40, there is no appreciable ion-pair formation. Inasmuch as the dielectric constant of monoethanolamine is comparatively high (37·72 at 25° C.), the non-appearance of a conductance minimum for sodium nitrite in it, seems reasonable.

## Summary

1. Solubilities of nitrites of sodium, potassium and silver have been determined in anhydrous ethylenediamine and monoethanolamine.

2. Silver nitrite forms a crystalline solvate with ethylenediamine with this formula $AgNO_2 \cdot 2\,[C_2H_4(NH_2)_2]$.

3. The ethylenediamine solutions of silver and sodium nitrites are more conducting than those of monoethanolamine; however, potassium nitrite behaves contrary to the above trend.

4. Sodium nitrite shows a conductance minimum in ethylenediamine but not in monoethanolamine. Such behaviour has been encountered in ethylenediamine with mercuric cyanide[13].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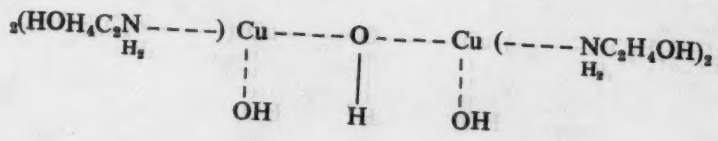
## ERRATUM

Vol. XLVI, No. 5, page 386, read the structure of the complex as follows:—



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